

A., II.—Organic Chemistry

JANUARY, 1938.

Natural products and synthetic products. G. BRUNI (Chim. e l'Ind., 1937, 19, 621—628).—A lecture.

Application of volume relationships to the elucidation of the constitution of organic liquids. F. WRATSCHKO (Österr. Chem.-Ztg., 1937, 40, 489—497).—An attempt is made to apply the deviations of the mol. volume from additivity to the determination of constitution and, particularly, to the elucidation of the no. of independent ring systems. A "characteristic" (Q) is defined which is const. in homologous series and characteristic thereof, and an additional factor η for compounds which contain other elements in addition to C and H. (Q) is expressed by the total no. of atoms, n , or valencies, v , the no. (C) of the atoms which are directly concerned with eventual ring formation (these-called nuclear elements), and K , the no. of independent ring systems, *i.e.*, those which do not have a common nuclear element. To separate homologous series with the same characteristic it is expedient to plot (Q) as ordinate against a function $A = 12 - (Q) + v - 2n$ as abscissæ for definite vals. of K . A typical series of graphs is given for $K = 1$ and the vals. of (Q), $v - 2n$, C , and K are quoted for a large no. of homologous series and for individual elements and groups. Characteristic n vals. according to the type of linking are given. Numerous examples are cited which establish the possibility of the attempt. Deviations are observed with about the first four members of a homologous series. Further the triple linking usually appears as a three-membered ring. Unusual deviations are found in C_6H_6 derivatives with $>$ three side-chains; it appears as if for additional side-chains 1—2 C atoms entered into the ring. H. W.

Hydroxylation of unsaturated substances. III. Use of vanadium pentoxide and chromium trioxide as catalysts of hydroxylation. N. A. MILAS. IV. Catalytic hydroxylation of unsaturated hydrocarbons. N. A. MILAS and S. SUSSMAN (J. Amer. Chem. Soc., 1937, 59, 2342—2344, 2345—2347; cf. A., 1936, 1091; 1937, II, 175). III. H_2O_2 and CrO_3 or, better, V_2O_5 convert $CMe_2:CHMe$ into $OH\cdot CMe_2\cdot CHMe\cdot OH$, Et_2 fumarate into Et_2 *r*-tartrate, anethole into $OMe\cdot C_6H_4\cdot CHO$, isoeugenol into vanillin, isosafrole into piperonal, C_6H_6 into $PhOH$, cyclohexene into adipic acid with small amounts of *cis*-cyclohexane-1:2-diol and an aldehyde, $PhMe$ into cresols, and $C_{10}H_8$ into naphthols. Peracids are formed from the inorg. oxides.

IV. H_2O_2 and OsO_4 give the following from the appropriate unsaturated compound, *cis*-glycols being

formed in all cases: $(CH_2\cdot OH)_2$, $OH\cdot CHMe\cdot CH_2\cdot OH$ (68%), cetene glycol (77.82%), $OH\cdot CHPh\cdot CH_2\cdot OH$ (56%), $OH\cdot CHEt\cdot CHMe\cdot OH$ (26—30%), $OH\cdot CMeEt\cdot CH_2\cdot OH$, b.p. $188^\circ/760$ mm., 111 — $114^\circ/37$ mm. (52%) [*3-nitrophthalate*, m.p. 199.8° (corr.)], $(CHEt\cdot OH)_2$ (36%), cyclohexane-1:2-diol, hexane- $\alpha\beta\zeta$ -tetraol (42%), and *p*-menthane-1:2:8:9-tetraol (from *d*-limonene) (35%). C_6H_6 gives 23% of $PhOH$. R. S. C.

cis- and *trans*-Isomerides of Δ^6 -pentene. (MISSIS) M. L. SHERRILL and E. S. MATLACK (J. Amer. Chem. Soc., 1937, 59, 2134—2138).—*cis*- (I) and *trans*- Δ^6 -Pentene (II) are prepared pure. Prep. of mixtures is also described. $CHMe\cdot CEt\cdot CO_2H$ (modified prep.), m.p. 40 — 41° , gives β -iodo- α -ethylbutyric acid, m.p. 29.5 — 30° , which with 0.2 mol. of Na_2CO_3 gives (II), b.p. 36.25° , n_D^{20} 1.3790, d_4^{20} 0.6486, but in quinoline gives 85—90% pure (I). $\beta\gamma$ -Dibromopentane, b.p. 62.5° , with $KOH\cdot EtOH$ gives 80% of Δ^6 -pentinene, b.p. 55° , which with H_2 -colloidal Pd in aq. $EtOH$ yields (I), b.p. 37.8° , d_4^{20} 0.6586, n_D^{20} 1.3822. $CHMeBr\cdot CHEt\cdot OEt$ and $CHEtBr\cdot CHMe\cdot OEt$ with Zn give the same mixture containing 55—60% of (I), whilst the mixture from $CHEt_2\cdot OH$ and 9M- H_2SO_4 contains 25% of (I). Results of other workers are discussed. R. S. C.

Rearrangement of acetylenes into allenes at high temperature. C. D. HURD and R. E. CHRIST (J. Amer. Chem. Soc., 1937, 59, 2161—2165).— C_3H_6 , CH_4 , and C_2H_4 , with a little C_2H_6 and H_2 , but only traces of acetylenes, are formed by pyrolysis of Δ^4 -hexinene and -heptinene (I) at 500° , 550° , or 600° . Δ^6 -Hexa- and -hepta-diene, respectively, are the chief liquid products; conjugated and aromatic hydrocarbons are absent, but a small amount of pentenes and hexenes is formed from (I), with traces of Δ^6 -hexinene or -heptinene at 600° . The structure of the allenes is established by ozonolysis. Decomp. and isomerisation begin at the same temp. Formation of radicals and a chain mechanism are postulated and discussed. R. S. C.

Relation between refraction data and reactivity of halogenated methane derivatives.—See A., 1937, I, 601.

Preparation of alkyl halides of higher mol. wt. A. GUYER, A. BIELER, and E. HARDMEIER (Helv. Chim. Acta, 1937, 20, 1462—1467).—The optimum temp. for the reaction between cetyl alcohol (I) and HCl is 160 — 170° . At 160° the rate of reaction increases with addition of $ZnCl_2$ by $\sim 100\%$; greater addition does not cause increased acceleration. Replacement of $ZnCl_2$ by $CdCl_2$, $SnCl_2$, $AlCl_3$, $CuCl_2$,

FeCl_3 , H_2SO_4 , ZnSO_4 , Na_2SO_4 , CuSO_4 , or MgSO_4 shows that Zn salts have a sp. effect particularly marked with ZnCl_2 . CdCl_2 has some activity but the remaining compounds are inactive or nearly so. Reaction between (I) and HBr is almost quant. at 150° in absence of catalyst. Gradual heating of (I) with 55% HI to 120° affords cetyl iodide in nearly quant. yield. Under precisely similar conditions the cetyl halides are formed in 97.0–99.2% yield from cetyl stearate. H. W.

Fluorinated derivatives of propane. A. I. HENNE and (Miss) M. W. RENOLL (J. Amer. Chem. Soc., 1937, 59, 2434–2436).— CMe_2Cl_2 reacts rapidly and completely with SbF_5 to give $\beta\beta$ -difluoropropane, b.p. -0.6° to -0.2° , with 5–7% of β -chloro- β -fluoropropane, b.p. 35.2° ; addition of 5% of Br catalyses the reaction, but SbCl_5 makes it violent. Fluorination of CMe_2ClBr is equally simple, but that of $\text{CMeClBr}\cdot\text{CH}_2\text{Br}$ and $(\text{CMeBr})_2$ is, as anticipated, troublesome. Chlorination of CMe_2ClF is accompanied by fission, leading to $\text{CCl}_2\text{F}\cdot\text{CCl}_3$; that of CMe_2F_2 is homogeneous and asymmetric, leading to α -chloro-, b.p. 55.1° , $\alpha\alpha$ -di-, b.p. 78.5 – 79.5° , $\alpha\alpha\alpha$ -tri-, b.p. 102° , m.p. 47 – 49° , $\alpha\alpha\alpha\gamma$ -tetra-, b.p. 151° , penta-, b.p. 174° , and hexa-chloro- $\beta\beta$ -difluoropropane, b.p. 194 – 194.4° , m.p. -15.8° . The following are also prepared: β -chloro- α -bromo- β -fluoro-, b.p. 110 – 112° , α -bromo- $\beta\beta$ -difluoro-, b.p. 76.2 – 76.3° , $\alpha\alpha$ -dichloro- $\alpha\beta\beta$ -trifluoro-, b.p. 60 – 60.3° , and $\alpha\alpha\alpha\gamma\gamma$ -pentachlorotrifluoro-propane, b.p. 152 – 154° . Analysis of the high-boiling substances is possible only by Carius' method, which, however, is always slow (7 days at 250 – 300°) and not always trustworthy. R. S. C.

Allylic rearrangements. VI. Effect of solvent and metal on the coupling reaction of butenyl bromides. W. G. YOUNG, J. F. LANE, A. LOSHOKOV, and S. WINSTEIN (J. Amer. Chem. Soc., 1937, 59, 2441–2443; cf. A., 1937, II, 480).—The yield of Grignard reagent from a mixture of 87% of $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ and 13% of $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\text{Br}$ in R_2O is $\text{Et}_2\text{O} > \text{Pr}^i_2\text{O} > \text{Pr}^n_2\text{O} > \text{Bu}_2\text{O}$. In pure Pr^n_2O no reaction occurs, and the above-mentioned ratio refers to 90% $\text{Pr}^n_2\text{O} + 10\%$ of Et_2O . In all cases 100% yield is obtained by using sufficiently dil. solutions. The yield of coupled product using Zn in 80% EtOH is decreased by vigorous stirring and/or increasing the dilution. With Zn, Al–Hg, Cr, or Sn (50-mesh) in 80% EtOH butene is the chief product, but with Mg, Na, Fe, Mn, Sn turnings, Cu, Ag, Cd, or Raney Ni mainly or only coupling occurs; Co does not react. R. S. C.

Aliphatic nitro-compounds. V. Oxidising action of bromonitro-methanes and -ethanes. N. N. MELNIKOV (J. Gen. Chem. Russ., 1937, 7, 1546–1552).— $\text{CH}_2\text{Br}\cdot\text{NO}_2$ (I) reacts with RSH ($\text{R} = \text{Ph}$, $\text{C}_6\text{H}_5\text{Me}$) in KOH – EtOH as follows: $\text{RSK} + (\text{I}) \rightarrow \text{SR}\cdot\text{CH}_2\cdot\text{NO}_2 + \text{KBr}$; $2\text{SR}\cdot\text{CH}_2\cdot\text{NO}_2 \rightarrow \text{R}_2\text{S}_2 + 2\text{CO} + \text{N}_2 + 2\text{H}_2\text{O}$. The corresponding reactions with $\text{CHBr}_2\cdot\text{NO}_2$ (II) are: $2\text{RSK} + (\text{II}) \rightarrow (\text{SR})_2\text{CH}\cdot\text{NO}_2$ (III) + 2KBr ; $2(\text{III}) \rightarrow \text{R}_2\text{S}_2 + \text{H}_2\text{O} + \text{CO} + \text{CO}_2 + \text{N}_2$; $4(\text{III}) \rightarrow 4\text{R}_2\text{S}_2 + 2\text{H}_2\text{O} + 4\text{CO} + \text{N}_2 + 2\text{NO}$; with $\text{CHMeBr}\cdot\text{NO}_2$ (IV): $2\text{RSK} + (\text{IV}) \rightarrow \text{SR}\cdot\text{CHMe}\cdot\text{NO}_2$ (V) + 2KBr ; $2(\text{V}) \rightarrow \text{R}_2\text{S}_2 + \text{N}_2 + 2\text{AcOH}$, and with $\text{CMeBr}_2\cdot\text{NO}_2$ (VI):

$2\text{RSK} + (\text{VI}) \rightarrow (\text{SR})_2\text{CMe}\cdot\text{NO}_2$ (VII) + SKBr ; $2(\text{VII}) + 2\text{RSK} \rightarrow 3\text{R}_2\text{S}_2 + 2\text{KOAc} + \text{N}_2$. The following reactions with PPh_3 are established: $\text{PPh}_3 + (\text{I}) \rightarrow \text{PPh}_3\text{Br}\cdot\text{CH}_2\cdot\text{NO}_2$ (VIII); $\text{PPh}_3\text{O} + 2\text{HBr} + 2\text{CO} + \text{N}_2 + \text{H}_2\text{O} \leftarrow (\text{VIII}) + (\text{I}) \rightarrow \text{PPh}_3\text{Br}_2$ (IX) + $2\text{CO} + \text{N}_2 + 2\text{H}_2\text{O}$; $\text{PPh}_3 + (\text{II}) \rightarrow \text{PPh}_3\text{Br}\cdot\text{CHBr}\cdot\text{NO}_2$ (X); $2(\text{X}) \rightarrow 2(\text{IX}) + \text{H}_2\text{O} + \text{CO} + \text{CO}_2 + \text{N}_2$; $4(\text{X}) \rightarrow 2\text{PPh}_3\text{O} + 4\text{HBr} + 2(\text{IX}) + 4\text{CO} + 2\text{NO} + \text{N}_2$; $\text{PPh}_3 + (\text{IV}) \rightarrow \text{PPh}_3\text{Br}\cdot\text{CHMe}\cdot\text{NO}_2$ (XI); $(\text{XI}) + (\text{IV}) \rightarrow (\text{IX}) + 2\text{AcOH} + \text{N}_2$; $\text{PPh}_3 + (\text{VI}) \rightarrow \text{PPh}_3\text{Br}\cdot\text{CMeBr}\cdot\text{NO}_2$ (XII); $4(\text{XII}) \rightarrow 4(\text{IX}) + 2\text{Ac}_2\text{O} + \text{N}_2 + 2\text{NO}$. R. T.

Mechanism of oxidation of organic compounds with selenium dioxide. I. Oxidation of alcohols. N. N. MELNIKOV and M. S. ROKITSKAJA (J. Gen. Chem. Russ., 1937, 7, 1532–1538).—The reactions between SeO_2 and alcohols are as follows: $\text{CH}_2\text{R}\cdot\text{OH} + \text{SeO}_2 \rightarrow (\text{CH}_2\text{R})_2\text{SeO}_3$ (I) + H_2O ; (I) $\rightarrow 2\text{R}\cdot\text{CHO} + \text{H}_2\text{O} + \text{Se}$; (I) + $2\text{H}_2\text{O} \rightarrow 2\text{CH}_2\text{R}\cdot\text{OH} + \text{H}_2\text{SeO}_3$. The following esters, R_2SeO_3 , are prepared by boiling the appropriate alcohol with SeO_2 , filtering, and fractionally distilling the filtrate: $\text{R} = \text{Me}$, Et , Pr , Bu^a , Bu^b , b.p. 113 – $117^\circ/5$ mm., and isomyl, b.p. 130 – $131^\circ/6$ mm. The esters decomposed when heated, to yield the appropriate aldehydes. R. T.

Application of L. A. Tschugaev's xanthate method to dihydric alcohols. V. E. TSCHITSCHENKO and A. F. KOSTERNAJA (J. Gen. Chem. Russ., 1937, 7, 1366–1377).— $(\cdot\text{CH}_2\cdot\text{ONa})_2$ is heated with CS_2 in EtOH at 70° for 24 hr., and MeI is added, when $(\text{CH}_2\cdot\text{S})_2\text{CS}$ and $(\cdot\text{CH}_2\cdot\text{MeCS})_2$ are obtained. Na_2COS_2 in EtOH and $(\text{CH}_2\text{Br})_2$ yield $(\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{OEt})_2$, which gives C_2H_2 , COS , and EtSH when heated at 200 – 260° . $\text{CHMeBr}\cdot\text{CH}_2\text{Br}$ similarly affords $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$, converted at 270° into $\text{CH}\cdot\text{CMe}$, whilst $(\cdot\text{CHMe}\cdot\text{S}\cdot\text{CS}\cdot\text{OEt})_2$ gives $(\text{CH}_2\cdot\text{CH}\cdot)_2$ under similar conditions. R. T.

Ether-like compounds. XVIII. Di-ethers of diprimary glycols. M. H. PALOMAA and I. HONKANEN (Ber., 1937, 70, [B], 2199–2205; cf. A., 1936, 966; Löbeking and Fleischmann, A., 1937, I, 399).—The production of azeotropic mixtures is a common property of acetals. Pure methylal is readily obtained by keeping the distilled crude product in contact with CaCl_2 , Na_2CO_3 , and Na successively and finally distilling with aid of a diplegmator. The errors involved in measuring the rate of hydrolysis of methylal are discussed. The following ethers have been obtained according to the scheme: $\text{OR}\cdot[\text{CH}_2]_2\cdot\text{OH} \rightarrow \text{OR}\cdot[\text{CH}_2]_2\cdot\text{ONa} \rightarrow \text{OR}\cdot[\text{CH}_2]_2\cdot\text{OR}'$; $(\text{CH}_2\cdot\text{OMe})_2$, b.p. 84.7 – $84.8^\circ/760$ mm.; α -methoxy- β -ethoxyethane, b.p. 101.5 – $102^\circ/758$ mm.; α -methoxy- β -n-propylethane, b.p. $124.5^\circ/759$ mm. H. W.

Preparation of cyclic acetals. T. BERSIN and G. WILLFANG (Ber., 1937, 70, [B], 2167–2173).—A mixture of the requisite aldehyde with a 10% excess of the ethylene oxide, usually epichlorohydrin, is added gradually and with good stirring to a dil. solution of the catalyst, usually SnCl_4 , in CCl_4 . If the temp. of the mixture falls, a further small portion of catalyst is added. After a short time at

room temp. the mixture is poured into 2N-NaOH. γ -Chloropropylene acetals of the following aldehydes are described which are probably mixtures of isomerides since the b.p. are not well defined even after protracted purification: EtCHO, b.p. 65–70°/18 mm.; PrCHO, b.p. 78.5–85°/14 mm.; octaldehyde, b.p. 109–117°/5 mm. (octaldehydesemicarbazone, m.p. 98°); decaldehyde, b.p. 142–148°/about 4 mm.; dodecaldehyde, b.p. 170–179°/4 mm. H. W.

Synthesis of choline and aminoethyl esters of ethyl orthophosphate. T. L. McMEEKIN (J. Amer. chem. Soc., 1937, 59, 2383–2384).— P_2O_5 and Et_2O give mainly $EtPO_3$ (with some $Et_2P_2O_7$), which with $CH_2Cl \cdot CH_2 \cdot OH$ gives *Et* β -chloroethyl *H* orthophosphate (*Ba* salt), and this with NEt_3 gives *Et* choline orthophosphate, $OEt \cdot PO(O \cdot O \cdot O \cdot [CH_2]_2 \cdot NMe_3^+ (HgCl_2 \text{ derivative, m.p. } 180\text{--}185^\circ, \text{ of variable composition; flavianate, m.p. } 155^\circ \text{ after softening at } 130^\circ), \text{ or with } NH_3, \text{ Et } \beta\text{-aminoethyl orthophosphate, m.p. } 228\text{--}230^\circ \text{ (flavianate, softens at } 120^\circ, \text{ m.p. } 160^\circ).$ R. S. C.

Syntheses of mercury methyl- and ethylthiocarbonates. H. S. FRY and J. B. CALLAWAY (Rec. trav. chim., 1937, 56, 1153–1160).— HCO_2Et and HCO_2Me , with CS_2 and HgO in H_2O yield respectively $(CO_2Et \cdot CS_2)_2Hg$, m.p. 64.5–65°, and *Hg Me*₂ thiocarbonate, m.p. 93–93.5°, which, treated with aq. NH_3 , yield $EtOH$ and $MeOH$, respectively, with HgS , $(NH_4)_2S$, and $CO(NH_2)_2$. J. D. R.

Preparation of purest acetic acid. K. HESS and H. HABER (Ber., 1937, 70, [B], 2205–2209).—Application of desiccating agents is not advantageous and distillation and partial freezing are the only methods available for preparing acid of the highest purity. A first fractional distillation with simple apparatus can be applied to the technical acid with m.p. 15.00–16.45°. This is followed by a second fractional distillation with special still-head for which samples with m.p. 16.45–16.59° are suitable. For two partial freezings the samples should have m.p. 16.59–16.635°. The purest $AcOH$ has m.p. $16.635 \pm 0.002^\circ$. It is very hygroscopic and requires special modes of transference. In practice the twice-distilled acid should be preserved and partly frozen immediately prior to use. H. W.

Kinetics of polymerisation. A. C. CUTHBERTSON, G. GEE, and E. K. RIDEAL (Nature, 1937, 140, 889).—Aldehyde-free vinyl acetate (I) does not polymerise at 100° even in presence of O_2 . Samples of (I) that polymerise always gave a test for a peroxide and the rate and extent of polymerisation \propto the amount present. The discrepancies in the findings of various authors in this and in the polymerisation of styrene may be explained by the presence of a peroxide catalyst. L. S. T.

Highly unsaturated fatty acid $C_{24}H_{38}O_2$ from the oil of the tunny, *Tyrmus tyrmus*, L. S. UENO and S. TAKASE (Bull. Chem. Soc. Japan, 1937, 12, 453–455).—The acid $C_{24}H_{38}O_2$, isolated from tunny oil as its *Me* ester, b.p. 224–226°/3 mm., when ozonised yields $MeCHO$, $EtCHO$, CO_2 , and $(CH_3 \cdot CO_2H)_2$. It therefore contains the groups CH_2Et , $\cdot CH \cdot CH_2 \cdot CH \cdot$ or $\cdot CH \cdot CH_2 \cdot CO_2H$, and $\cdot CH \cdot CH_2 \cdot CH_2 \cdot CH \cdot$ or $\cdot CH \cdot CH_2 \cdot CH_2 \cdot CO_2H$. A. LI.

Oxidation of α -hydroxy-acids. W. CIUSA (Atti R. Accad. Lincei, 1937, [vi], 25, 632–637).—The oxidation of $OH \cdot CR_2 \cdot CO_2H$ to $COR_2 + CO_2$ is considered to pass through an intermediate stage $CR_2 \cdot \begin{smallmatrix} O \\ \diagup \diagdown \\ CO \end{smallmatrix} \cdot O$. If this is correct, $OH \cdot CHMe \cdot CO_2Et$ would be expected to yield $AcCO_2Et$ in much greater proportion than $AcCO_2H$ from $OH \cdot CHMe \cdot CO_2H$, and in fact the relative yields are 33 : 13% using $Br \cdot H_2O$, and 9 : 0.5% using $KOBr$. E. W. W.

Monoalkyl carbonates. VI. Alkyl carbonate of lactic acid. C. FAURHOLT, K. NOIESEN, and F. RATH (Dansk Tidsskr. Farm., 1937, 11, 267–277).—The ion $CO_2' \cdot CHMe \cdot O \cdot CO_2'$ (I) is formed on passing CO_2 into an aq. solution of $NaOH$ and $OH \cdot CHMe \cdot CO_2H$ (II), and from aq. $NaHCO_3$ and aq. (II). The equilibrium consts. have been measured. In alkaline solution (I) decomposes in two stages: (I) $\rightarrow O' \cdot CHMe \cdot CO_2'$ (III) + CO_2 , followed by: (III) + $H_2O \rightarrow OH \cdot CHMe \cdot CO_2' + OH'$. M. H. M. A.

β -Pivalylpropionic acid and its derivatives. G. A. HILL, V. SALVIN, and W. T. M. O'BRIEN, jun. (J. Amer. Chem. Soc., 1937, 59, 2385–2386).— $CH_2(CO_2Et)_2$ and $COBu' \cdot CH_2Br$ in $EtOH$ at 50° give *Et*₂ β -pivalylmalonate, b.p. 151–152°/10 mm., hydrolysed by KOH to the corresponding acid, m.p. 136° (*Ca* and *Ag*₂ salts), which at 140° gives CO_2 and β -pivalylpropionic acid (I), m.p. 69° (oxime, m.p. 141°; *Me*, b.p. 180°/9 mm., and *Et* ester, b.p. 118°/9 mm.; amide, m.p. 129°). At 250°/760 mm. the acid yields γ -tert.-butylcrotonolactone, b.p. 220°, which gives the amide of (I), yields $\alpha\beta$ -dihydroxy- γ -tert.-butylbutyrolactone, m.p. 132°, with $KMnO_4 \cdot MgSO_4 \cdot COMe_2$, and with $H_2 \cdot PtO_2$ in $EtOH$ gives γ -tert.-butylbutyrolactone, b.p. 112°/12 mm., unchanged by $H_2 \cdot PtO_2$, HI , HI -red P, or PCl_5 . Only $Na \cdot Hg$ reduces (I). R. S. C.

Ammine complexes of the salts of adipic acid with heavy metals. A. MARITZ (Helv. Chim. Acta, 1937, 20, 1575–1578).—The following complex salts, $[Cu(NH_3)_2]C_6H_8O_4 \cdot H_2O$; $[Ca(C_5H_5N)_2]C_6H_8O_4$; $[Cd(NH_3)_2]C_6H_8O_4$; $[Cd(C_5H_5N)_2]C_6H_8O_4$; $[Zn(NH_3)_2]C_6H_8O_4 \cdot H_2O$; $[Zn(C_5H_5N)_2]C_6H_8O_4$; $[Ni(NH_3)_2]C_6H_8O_4$; and $[Ni(C_5H_5N)_2]C_6H_8O_4$, prepared from the metallic adipate and NH_3 or C_5H_5N , are somewhat unstable, in which respect they resemble analogous succinates. H. W.

0-Dihydroxystearic acids in relation to oleic and elaidic acid. V. I. ESAFOV (J. Gen. Chem. Russ., 1937, 7, 1403–1412).—The iodohydrin of oleic acid (I) yields chiefly *trans*-dihydroxystearic acid (II) when heated at 100° with 2.5% KOH ; the proportion of *cis*-isomeride (III) in the product rises with increasing $[KOH]$, to the complete absence of (II) when 45% KOH is used. In the case of elaidic acid (IV), (II) is the main product with low $[KOH]$, whilst at higher $[KOH]$ it consists chiefly of the oxide (V) of (IV), pointing to the *cis*-configuration of the iodohydrin of (IV); (II) is a secondary product formed by hydration of (V). It is concluded that the configuration of (II) corresponds with that of (I), and of (III) with (IV). R. T.

Catalytic reduction of the methyl ester of 2:3:4-triacetyl- α -methylgalacturonide to methyl-*d*-galactoside. P. A. LEVENE and C. C. CHRISTMAN (Science, 1937, 86, 381).—This has been effected (cf. A., 1937, I, 484). L. S. T.

Alginic acid. E. HEEN (Tids. Kjemi, 1937, 17, 127—129).—Analysis of Na alginate, evolution of CO₂ from alginic acid (I), and direct titration of (I) confirm its composition as (C₆H₈O₆)_n. Treatment of (I) with MeOH-HCl, followed by hydrolysis, yields two fully methylated products with $n = 5$ and $n = 15$, the mol. wt. being confirmed cryoscopically. Viscosimetric measurements with (I) in aq. NaOH give mol. wt. of 15,000 ($n = 80$). Threads prepared from solutions of (I) give a typical X-ray fibre diagram. It is concluded that (I) consists of condensed hexuronic (probably mannuronic) acid residues, having a structure very like that of cellulose, but with CO₂H replacing CH₂·OH. It can be considered as a link between the homopolar celluloses and the heteropolar proteins. M. H. M. A.

Transformation of an isocarboxylic acid into a carboxylic acid. H. J. BACKER and J. STRATING (Rec. trav. chim., 1937, 56, 1133—1138).—The transformation of trimethylacetonylsulphonyl-methane-isocarboxylic acid, COBu^γ·CH₂·SO₂·CH₂·CHO₂ (I) (cf. A., 1935, 498), into the -acetic acid (II) in H₂O is a unimol. reaction. Salts of (I) with the following bases are described: NH₂Bu^γ, m.p. 140—141° (decomp.), NHMe₂, m.p. 110—111° (decomp.), piperidine, m.p. 123—124° (decomp.), and pyridine, m.p. 53—55° (decomp.); these are identical with the salts formed from (II) and the appropriate base. Salts of (II) with the following bases are also described: NH₂Ph, m.p. 93—94° (decomp.), NHPHEt, m.p. 124—125° (decomp.) α -C₁₀H₇·NH₂, m.p. 105·5—106·5° (decomp.), and β -C₁₀H₇·NH₂, m.p. 135—136° (decomp.). J. D. R.

Kinetics of polymeric aldehydes. VIII. Stepwise mechanism of the hydrolysis of dissolved polyoxymethylene dimethyl ethers. J. LÖBERING and V. RANK (Ber., 1937, 70, [B], 2331—2339; cf. A., 1937, 399).—Attempts to deduce the rate of hydrolysis, k_m , of a mixed acetal (OMe·CH₂·OEt) from those, k_{SM} and k_{SE} , of the simple acetals CH₂(OMe)₂ and CH₂(OEt)₂ according to $k_{SM} - k_{SE}/2 = k_m$ are not usually successful and better agreement between theory and practice is obtained from $k_m = \sqrt{(k_{SM}k_{SE})}$. This relationship is extended and applied with satisfactory results to a series of more complex examples. H. W.

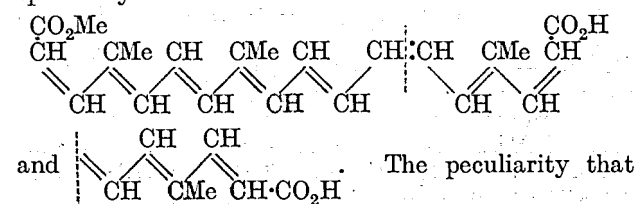
Keten acetals. II. Bromoketen diethyl acetal. Reactivity of bromo- and iodo-ethoxyacetal. F. BEYERSTEDT and S. M. McELVAIN (J. Amer. Chem. Soc., 1937, 59, 2266—2268; cf. A., 1936, 588).—Attempts to prepare [C(OEt)₂]₂ failed. Keten acetals boil at higher temp. than the corresponding esters, the difference in b.p. being less with increasing mol. wt. Scheibler's keten acetals cannot, therefore, have had the supposed structure. CH₂Br·CH(OEt)₂ and Br at 10—15° give the $\beta\beta$ -dibromoacetal, b.p. 94—97°/12 mm., which with KOEt gives 62·5% of β -bromo- β -ethoxyacetaldehyde Et₂ acetal (I), b.p. 77—

78°/12 mm., and a little CH₂Br·C(OEt)₃; the latter product is formed by way of bromoketen Et₂ acetal, b.p. 72—74°/9 mm., which is formed in 82% yield by the use of KOBu^γ. With KI (I) gives β -iodo- β -ethoxyacetaldehyde Et₂ acetal, b.p. 95—97°/12 mm., which reacts with KOBu^γ only at a temp. at which resinification of the product occurs. R. S. C.

Catalytic properties of rhenium. V. Dehydration of butyl alcohols. M. S. PLATONOV and S. B. ANISIMOV (J. Gen. Chem. Russ., 1937, 7, 1360—1363).—High yields of aldehydes are obtained from Bu^oOH or Bu^oOH with Re catalysts at 250—400°. R. T.

Composition of "Schunguli" oil. M. A. ISKENDEROV (J. Appl. Chem. Russ., 1937, 10, 1450—1456).—The essential oil obtained from the plant, which grows wild in Turkmenistan, before ripening of the seeds consists chiefly of the aldehydes α -methyl-dodec- Δ^6 -enal (I), b.p. 118—124°/10 mm. (semicarbazone, m.p. 158°; oxime, m.p. 79—80°), Δ^6 -tridecenal (II), b.p. 115—118°/10 mm. (semicarbazone, m.p. 155°; oxime, m.p. 84°), and trideca- $\Delta^{6,7}$ -dienal (III), b.p. 135—137°/10 mm. (semicarbazone, m.p. 160°; oxime, m.p. 73°). (I) yields α -methyl- Δ^6 -dodecenoic acid, m.p. 18·5°, when oxidised with AgOH, and *n*-decoic, oxalic, and formic acid with KMnO₄. (II) is oxidised (KMnO₄) similarly to undecic and oxalic acid, and (III) to $\Delta^{6,7}$ -trideca-dienoic acid, m.p. 10·5—11° (AgOH), or to nonoic and oxalic acid (KMnO₄). The oil obtained after ripening of the seeds consists of α -pinene 78, camphene 10, aldehydes 4, phenols 1, and EtOH + Et₂O 3%. The results suggest that terpenes are in this case formed from the aldehydes. R. T.

Stereochemistry of carotenoids. Stepwise degradation of labile and stable bixin. P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1937, 20, 1396—1407).—Oxidation of labile bixin Me ester in C₆H₆ by KMnO₄ and NaHCO₃ in H₂O at room temp. gives mainly apo-1-norbixinal Me ester (I), R·CH:CH·CH·CMe·CHO (R = CO₂Me·[CH:CH·CMe·CH]₂·CH:CH·CH:CH·CMe), m.p. 156° (oxime, m.p. 186°; semicarbazone, m.p. about 225°), a little non-cryst. labile apo-2-norbixinal Me ester (II), R·CH:CH·CHO, and apo-3-norbixinal Me ester (III), R·CHO, m.p. 147° (oxime, m.p. 188°; semicarbazone, m.p. 215°). These compounds are hydrolysed by KOH-EtOH to the corresponding aponorbixinals. Similar oxidation of stable bixin gives (III), small amounts of a stable apo-2-norbixinal Me ester differing from (II), and mainly stable apo-1-norbixinal Me ester (IV), m.p. 167°, which is stereoisomeric with (I), into which it is transformed by I. The isomerism of the bixins therefore depends on differing configuration around the double linking third from the unesterified CO₂H. The labile and stable forms may therefore be represented respectively



oxidation stops with the production of the aldehyde (not acid) is considered due to the comparative difficulty with which these complex aldehydes become hydrated. H. W.

Condensation reactions. I. Condensation of ketones with cyanoacetic esters. Mechanism of the Knoevenagel reaction. A. C. COPE (J. Amer. Chem. Soc., 1937, **59**, 2327—2330).—Acetates of bases, NH_4OAc and NH_2Ac , are better catalysts than are bases for the condensation of ketones with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$. With $\text{COMe}\cdot\text{C}_6\text{H}_{13}$ a 91% yield is obtained by using NH_2Ac (0.085 mol.) in AcOH and distilling the H_2O formed. The superiority of these catalysts depends on formation of basic and acidic ions and supports Hann and Lapworth's reaction mechanism. The following are prepared, usually in >70% yield: Me α -cyano- β -methylcrotonate, m.p. 20.3°, b.p. 99—101°/9 mm., Me α -cyano- β -methyl- Δ^2 -pentenoate, b.p. 105—106°/9 mm., -octenoate, b.p. 139—141°/9 mm., and -nonenoate, b.p. 149—152°/9 mm., α -cyano- β -ethyl- Δ^2 -pentenoate, b.p. 112—114°/9 mm., α -cyano- $\beta\delta$ -dimethyl-, b.p. 119—123°/9 mm., and - β -propyl- Δ^2 -hexenoate, b.p. 129—130°/9 mm., cyclo-pentylidene-, m.p. 31°, b.p. 140—141°/9 mm., and -hexylidene-cyanoacetate.

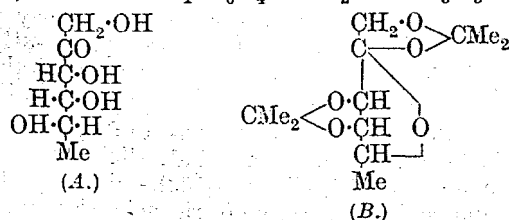
R. S. C.

Homogeneous l-erythrulose [l-2-ketotetrose]. H. MÜLLER, C. MONTIGEL, and T. REICHSTEIN (Helv. Chim. Acta, 1937, **20**, 1468—1473).—Oxidative fermentation of erythritol gives l-erythrulose (I), which, after purification through the o-nitrophenylhydrazone, m.p. 152—153° (corr.), $[\alpha]_D^{25} + 48 \pm 2^\circ$ in abs. EtOH, is a colourless syrup, $[\alpha]_D^{25} + 11.4 \pm 1^\circ$ in H_2O , which strongly reduces cold Fehling's solution and is very sensitive towards alkali. Its volatility without decomp. in a high vac. indicates that it exists mainly in the monomeric open-chain form (I). Attempts to obtain well-defined condensation products with COMe_2 or MeOH were unsuccessful.

The prep. of o- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ is described.

H. W.

d- and l-Tagatomethylose. J. BARNETT and T. REICHSTEIN (Helv. Chim. Acta, 1937, **20**, 1529—1536).—Partial isomerisation of l-fucose by boiling $\text{C}_5\text{H}_5\text{N}$ leads to l-tagatomethylose [l-lyxo-2-keto-5-methylpentose] (A), $[\alpha]_D^{25} + 2.68 \pm 0.4^\circ$ in H_2O , a syrup which slowly reduces cold Fehling's solution; it is isolated through its o-nitrophenylhydrazone (I), m.p. 161—162° (corr.), $[\alpha]_D^{25} - 69 \pm 5^\circ$ in MeOH. Tagatose is transformed by COMe_2 containing anhyd. CuSO_4 and conc. H_2SO_4 into the diisopropylidene derivative, which with p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ gives



1 : 2 : 3 : 4-diisopropylidene-d-tagatose 6-p-toluenesulphonate, m.p. 99—100° (corr.), $[\alpha]_D^{25} + 33.90 \pm 4^\circ$ in

COMe_2 . This is converted by NaI in COMe_2 at 100° into 6-iodo-1 : 2 : 3 : 4-diisopropylidene-d-tagatose, m.p. 43—44°, $[\alpha]_D^{25} + 61.6 \pm 4^\circ$ in COMe_2 , hydrogenated (Raney Ni in $\text{MeOH}\cdot\text{NaOH}$) to diisopropylidene-d-tagatomethylose (B), b.p. 73—75°/0.4 mm., m.p. 8.5—9°, $[\alpha]_D^{25} + 79.7 \pm 0.2^\circ$ in COMe_2 . This is hydrolysed by AcOH in H_2O -dioxan at 100° to d-tagatomethylose, $[\alpha]_D^{25} - 2 \pm 2^\circ$ in H_2O [o-nitrophenylhydrazone (II), m.p. 160—161° (corr.), $[\alpha]_D^{25} + 72.5 \pm 5^\circ$ in MeOH]. Admixture of equal amounts of (I) and (II) gives dl-tagatomethylose-o-nitrophenylhydrazone, m.p. 162—163° (corr.). The absence of depression of the f.p. indicates the formation of mixed crystals.

H. W.

Separation of inositol from glucose, and its determination. P. FLEURY and (MILLER) M. JOLY (J. Pharm. Chim., 1937, [viii], **26**, 341—353, 397—408).—Inositol (I) reduces > the theoretical amount of HIO_4 at room temp. in 24 hr. to give a solution having a small rotatory power and an analysis for 5 instead of 6 CO_2H groups. With excess of (I), 40% of HIO_4 disappears in 2 min. to give a solution with considerable rotatory power and strongly acid, probably due to the intermediate formation of an aldehyde and HCO_2H . Excess of HIO_4 completes the reaction as above. Small amounts of H_2SO_4 do not affect the reaction over a wide range of concns. of (I).

Glucose (II) is destroyed when an aq. solution of (II) and (I) is heated with freshly calcined MgO at 100°. (I), which is unaffected and can be obtained cryst., is determined after oxidation at room temp. with HIO_4 . HIO_4 oxidises (II) and (I) so that if the (II) content is determined (Fehling), (I) can be calc.

J. L. D.

Mutarotation of l-sorbose. W. W. PIGMAN and H. S. ISBELL (J. Res. Nat. Bur. Stand., 1937, **19**, 443—445).—Data obtained at 0.4° and 20° show that the optical rotation of l-sorbose in H_2O increases slightly at first and then decreases, the change being approx. 0.7° S. The solution at equilibrium is composed almost exclusively of that isomeride which is known in the cryst. state.

C. R. H.

l-Tagatose. C. GLATTHAAR and T. REICHSTEIN (Helv. Chim. Acta, 1937, **20**, 1537—1541).—l-Galactose is partly isomerised in $\text{C}_5\text{H}_5\text{N}$ and unchanged material is removed partly by direct crystallisation, partly after oxidation with Br to Ba galactonate. The residual syrup, particularly after being seeded with l-sorbose, gives l-tagatose (A), m.p. 134—135°, $[\alpha]_D^{25} + 1^\circ$ in H_2O . dl-Tagatose has m.p. 119—121°.

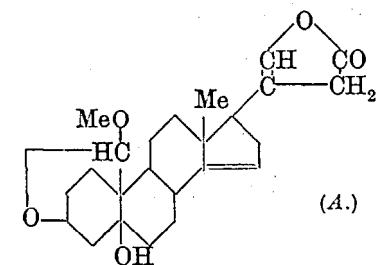
H. W.

Comparative study of determination of maltose by the gravimetric method with Fehling's solution, and by Bertrand's, Willstätter and Schudel's, and Bang's volumetric methods. A. TYCHOWSKI and J. PAJAK (Rocz. Chem., 1937, **17**, 383—386).—Bertrand's method is preferred.

R. T.

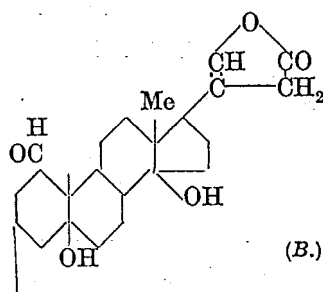
Heart glucosides. XIV. l-Strophanthoside, the chief glucoside of the seeds of Strophan-

thus kombé. A. STOLL, J. RENZ, and W. KREIS (Helv. Chem. Acta, 1937, 20, 1484—1510).—The fresh seeds are crushed with solid $(\text{NH}_4)_2\text{SO}_4$ and extracted with CHCl_3 -EtOH (5 : 2). The aq. solution of the extract after treatment with $\text{Pb}(\text{OH})_2$ is readily deprived of cymarin by extraction with CHCl_3 . *k*-Strophanthin- β is separated either by extraction with CHCl_3 in presence of EtOH and H_2O in defined amount or by addition of Et_2O to the solution in EtOH. The residual glucoside mixture (about 75% of the original material) is treated exhaustively with Ac_2O and $\text{C}_6\text{H}_5\text{N}$, giving *k*-strophanthoside heptaacetate, m.p. 229—230° (decomp.), $[\alpha]_D^{20}$ -4.56° in C_6H_6 , $+11.2^\circ$ in EtOH. Hydrolysis of this substance



(A.)

by HCl in abs. MeOH gives the methylsemiactal of oxidoanhydrostrophanthidin (A), $[\alpha]_D^{20}$ -38.8° in CHCl_3 (equilibrium val.). Alkaline hydrolysis readily gives *k*-strophanthoside (I), $\text{C}_{42}\text{H}_{64}\text{O}_{19}$, m.p. 199—200° (corr.; decomp.), $[\alpha]_D^{20}$ $+12.4^\circ$ in abs. EtOH, $+11.67^\circ$ in H_2O , $+13.85^\circ$ in MeOH. Acid hydrolysis of (I) gives strophanthidine in 46% yield and the sugar component is isolated intact as strophanthotriose (II), $\text{C}_{19}\text{H}_{34}\text{O}_{14}$, m.p. 222° (corr.; decomp.), $[\alpha]_D^{20}$ $+7.73^\circ$ in H_2O , whereas enzymic hydrolysis with the strophanthobiase of Jacobs leads to cymarin and glucose, the theoretical yield of the former being nearly attained. The



(B.)

O—cymarose—glucose—glucose

removal of the external glucose group solely is effected by the α -glucosidase of yeast. β -Glucosidases are without action on the new trioside so that the terminal glucose is in α -union with the remainder of the mol. (I) is therefore B. (II) reduces Fehling's solution but does not give a blue colour in the Keller-Kiliani reaction, showing the absence of free cymarose. It gives an octa-acetate, m.p. 192° (decomp.), $[\alpha]_D^{20}$ -6.16° in CHCl_3 , and a methylglucoside, $\text{C}_{20}\text{H}_{36}\text{O}_{14}$, m.p. 214° (corr.; decomp.), $[\alpha]_D^{20}$ $+1.06^\circ$ in H_2O . (I) appears to be a therapeutically valuable strophanthin prep. There is no evidence of the presence of further glucosides in *S. kombé*. H. W.

Oleandrin. G. HESSE (Ber., 1937, 70, [B], 2264—2267).—Oleandrin (I), m.p. 250° (decomp.), is $\text{C}_{32}\text{H}_{48}\text{O}_9$. It is converted at 260—330°/0.02 mm. into AcOH and deacetylanhydro-oleandrin $\text{C}_{30}\text{H}_{44}\text{O}_7$, m.p. 221°. Hydrolysis of (I) with N-HCl affords dianhydrogitoxygenin, m.p. 211—212°, and oleandrose (2 : 4-dinitrophenylhydrazones, decomp. 155—160°). Thermal decomp. of oleandrin yields AcOH and

anhydrogitoxygenin, so that the Ac of (I) is located in the genin residue. H. W.

Structure of cellulose. N. J. TOIVONEN (Suomen Kem., 1937, 10, A, 120—122).—A review.

Highly polymerised compounds. CLXXIX. Constitution of cellulose nitrates. H. STAUDINGER and R. MOHR [with, in part, H. HAAS and K. FEUERSTEIN] (Ber., 1937, 70, [B], 2296—2309).—The ease of production of complex cellulose nitrates (I) is due to their almost complete stability towards cold nitrating acid and the great rapidity with which they are formed so that the sensitive cellulose (II) is not long in contact with the acid. Conc. H_3PO_4 is more suitable than conc. H_2SO_4 as an addition to HNO_3 since it hydrolyses (II) less rapidly. For the study of (I) it is best to start with (II) repptd. from Schweitzer's solution and dried by successive treatments with EtOH, Et_2O , and cyclohexane; this is treated with HNO_3 (d 1.52), H_3PO_4 , 0.5 H_2O , and P_2O_5 at 0° for 12 hr. The val. of the K_m const. of (I) is amended to 11×10^{-4} ; the products used previously were to some extent degraded. (II) of differing degrees of polymerisation are thus esterified to polymeric-analogous products; under these conditions a rupture of the chain is not observed. Degradation is, however, obvious when HNO_3 - H_2SO_4 is used. The transformation of (I) into polymeric-analogous (II) has not been achieved; the best results are obtained by use of polysulphide or hydrosulphide but the products have a degree of polymerisation 120—300 whether or not meso- or eu-colloidal (I) are used as initial material. Nitration of native (II) and study of the viscosity of the products show that the material of cotton, flax, and other fibres has a degree of polymerisation of <3000 ; the long, thread-like macromols. have a length of 1.5 μ . H. W.

Reaction of amino-acids, peptides, and related substances with sugars. I. N. SHIGA (J. Biochem. Japan, 1937, 25, 607—626).— NH_2 -acids (glycine, ϵ -aminoheptanoic acid) combine, as indicated by NH_2 -N (Van Slyke), with glucose at p_H 7—9 to an extent increasing with p_H . With glycylglycine, combination at p_H 9 is $<$ that at p_H 7 and 8 for reaction periods of approx. 12 and 48 hr., respectively; the behaviour with *L*-leucylglycylglycine with respect to p_H is also anomalous. The combination with fructose is $<$ that with glucose. F. O. H.

Biuret reaction of the hexapeptide, pentaglycylglycine, and of the heptapeptide, hexaglycylglycine. (Miss) J. E. SAUERWEIN (J. Amer. Chem. Soc., 1937, 59, 2177—2178).—With $\text{Cu}(\text{OH})_2$ and NaOH pentaglycylglycine gives the derivative, $\text{C}_{12}\text{H}_{25}\text{O}_{12}\text{N}_6\text{CuNa}_3$, $+\text{H}_2\text{O}$ and $+\text{5H}_2\text{O}$, decomp. 259° (corr.). Hexaglycylglycine gives similarly the derivative, $\text{C}_{14}\text{H}_{23}\text{O}_{11}\text{N}_7\text{Cu}_2\text{NO}_4$, decomp. ($+\text{3H}_2\text{O}$) 275° or ($+\text{2EtOH}$) 271°. The structure of these derivatives is discussed. R. S. C.

Synthesis of γ -methylamino- and γ -methylguanido- β -hydroxybutyric acid. T. ISEKI (J. Biochem. Japan, 1937, 25, 549—553).— γ -2-Naphthalenesulphonamido- β -hydroxybutyric acid (Fukagawa, A., 1935, 610) with Me_2SO_4 in NaOH affords γ -2-naphthalenesulphonmethylamido- β -hydroxybutyric acid

m.p. 138—139°, hydrolysed (HCl) to γ -methylamino- β -hydroxybutyric acid, m.p. 190—191°, which with $\text{CN}\cdot\text{NH}_2$ yields γ -methylguanido- β -hydroxybutyric acid, m.p. 201—202° (hydrochloride, m.p. 170°).

F. O. H.

Action of chlorine on isothiocarbamides. III.

J. M. SPRAGUE and T. B. JOHNSON (J. Amer. Chem. Soc., 1937, 59, 2439—2441; cf. A., 1937, II, 480).—Aq. Cl_2 gives no sulphonyl chloride from $\text{CH}_2\text{R}\cdot\text{S}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$ when $\text{R} = \text{furyl}$ or OAlk , but $\text{S}\cdot\beta$ -acetoxyethylthiocarbamide (hydrochloride, m.p. 137—137.5°; picrate, m.p. 174.5—175.5°) gives a good yield of β -acetoxyethylsulphonyl chloride, b.p. 101—103°. Bis-($\text{S}\cdot\text{ethylisothiocarbamide}$) β -oxide, $\text{O}[\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}]_2$ [from $\text{O}(\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$] (picrate, m.p. 209—209.5°), gives Et_2 ether- $\beta\beta'$ -disulphonyl chloride, an oil (corresponding diamide, m.p. 125—126°). $\text{S}\cdot\text{Tetrahydrofurfurylisothiocarbamide}$ (picrate, m.p. 153—153.5°) gives tetrahydrofurfurylsulphonyl chloride, b.p. 112—113° (amide, m.p. 81.5—82.5°). 2:4-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{S}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$ gives 2:4-dinitrobenzenesulphonyl chloride, m.p. 101—102° (amide, m.p. 156—157°), but not smoothly. The following isothiocarbamides are described: $\text{S}\cdot\text{furfuryl}$ (picrate, m.p. 162°; hydrochloride, m.p. 142—143°), $\text{S}\cdot\text{methoxymethyl}$ (hydrochloride, m.p. 112°; picrate, m.p. 163°), $\text{S}\cdot\text{isoamyloxymethyl}$ (hydrochloride, m.p. 134—135°), $\text{S}\cdot\text{n-butoxymethyl}$ (hydrochloride, m.p. 118—120°), and $\text{S}\cdot\text{carbethoxymethyl}$ (hydrochloride, m.p. 112—113°). R. S. C.

β -Octylthiocarbamide. W. F. H. JACKMAN and J. KENYON (J. Amer. Chem. Soc., 1937, 59, 2473).— $\text{C}_8\text{H}_{17}\cdot\text{SCN}$ decomposes, when kept, as shown by change in d (redetermined). The following are re-calc.: $[\alpha]_{\text{D}}^{20} +62^\circ$, $[\alpha]_{\text{D}}^{20} +74.9^\circ$, $[\alpha]_{\text{D}}^{20} +121.5^\circ$. Walden inversion occurs in each reaction involving the asymmetric C of this compound, or the substances from which it is prepared. R. S. C.

Reactions of "thiuram sulphide." J. V. DUBSKÝ, A. LANGER, and A. OKÁČ (Coll. Czech. Chem. Comm., 1937, 9, 425—433).— $\text{CH}_2(\text{CN})_2$ in EtOH with H_2S under pressure yields thiomalonamide, m.p. 119° (Cu salt). The "thiuram sulphide" of Hlasiwetz and Kachler (A., 1873, 629) yields the following salts ($\text{R} = \text{NH}_2\cdot\text{CS}_2$): R_2Cd , R_2Pb , $(\text{RCu})_2\cdot\text{NH}_2\cdot\text{CS}_2\cdot\text{H}$, $\text{Bi}_2(\text{OH})\text{R}_5\cdot 3\text{H}_2\text{O}$, R_2Ni , $\text{R}_2\text{Co}\cdot 4\text{H}_2\text{O}$, R_2Zn , and an Fe salt of unknown composition. The same salts are formed from $\text{NH}_2\cdot\text{CS}_2\cdot\text{H}$. "Thiuram disulphide," from $\text{NH}_2\cdot\text{CS}_2\cdot\text{H}$, HCl , and FeCl_3 , yields no salts with Cu, Co, or Ni in COMe_2 , but in alkaline solution salts are formed with Co, Ni, Fe, Ag, Cu, Pb, Zn, Cd, Bi, Sb, and Sn. NiCl_2 , NH_3 , and CS_2 in H_2O yield a salt, $\text{Ni}(\text{NH}_3)_3\text{CS}_3$. J. D. R.

Reduction of nitroguanidine. X. Hydrolysis of aminoguanidine in acidic and basic media. XI. Reduction of γ -nitro- α -alkylguanidines. E. LIEBER and G. B. L. SMITH (J. Amer. Chem. Soc., 1937, 59, 2283—2287, 2287—2289; cf. A., 1937, II, 489).—X. $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{NH}_2$ (I) and $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ (II) are stable to dil. acid; in hot 3-924N- H_2SO_4 (II) is much more easily hydrolysed than (I). In $<0.2\text{N}\cdot\text{NaOH}$ (I) is hydrolysed faster than is (II), but in $>0.2\text{N}\cdot\text{NaOH}$ this relation is reversed. Probably (I) exists in acid as

$\text{NH}_2\cdot\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}_2^+$, as this accounts for hydrolysis to (II). Hydrogenation (PtO_2) of nitroguanidine to (I) at 25°, 75°, or 125° occurs much better in 15% AcOH than in H_2O .

XI. Hydrogenation (Raney Ni) of $\text{NHR}\cdot\text{C}(\text{NH})\cdot\text{NO}_2$ (III) ($\text{R} = \text{Me}$ or Et) in MeOH with or without alkali gives first the NO (IV) and then the NH_2 -derivatives. In acid solution (IV) appear not to be formed. Purification of (IV) is effected by way of their Ni derivatives, which are explosive and are analysed by decomp. with 3M- H_2SO_4 , followed by titration with KMnO_4 . The structure of (III) is confirmed by these reductions. R. S. C.

Carbamide series. XV. Transformations of nitrosoguanidine.

Alkyl nitrosoguanidines. NN' -Dialkylguanidines. T. L. DAVIS and E. N. ROSENQUIST (J. Amer. Chem. Soc., 1937, 59, 2112—2115; cf. A., 1937, II, 488).—Nitrosoguanidine (prep. by Zn dust and aq. NH_4Cl from nitroguanidine) (Ag salt) dissociates during reaction in H_2O mainly into $\text{NH}_2\cdot\text{CN}$ and $\text{NH}_2\cdot\text{NO}$, and partly into NH_3 and $\text{CN}\cdot\text{NH}\cdot\text{NO}$. With aq. NH_3 it gives 23—34% of guanidine with melamine (I), ammelide (II), etc. With aq. $(\text{NH}_4)_2\text{CO}_3$ at 70° it gives guanidine carbonate (80%) with (I) (2%) and (II) (6%). With the appropriate base in H_2O it gives methyl- (21.2%), ethyl- (16.9%), m.p. 175°, n -butyl- (35.9%), n -heptyl- (35.4%), NN -dimethyl- (21.4%), benzyl- [16.3% with much $\text{CO}(\text{NH}\cdot\text{CH}_2\text{Ph})_2$], and piperidino-guanidine (37.2%). $\text{N}\cdot\text{Nitroso-N}'\cdot\text{methyl}$, m.p. 95° (decomp.), unstable, $\text{N}'\cdot n$ -butyl- and $\text{N}'\cdot\text{benzyl-guanidine}$, oils (Ag salts), are similarly obtained and with the appropriate amine give 8—22% of NN' -dimethyl-, $\text{N}\cdot\text{methyl-N}'\cdot\text{ethyl}$ (picrate, m.p. 170—171°), n -butyl- (picrate, m.p. 139.5—141°), and n -benzyl- (picrate, m.p. 196—197°), $\text{N}\cdot\text{ethyl-N}'\cdot n$ -butyl- (picrate, m.p. 120°), $\text{N}\cdot\text{piperidino-N}'\cdot\text{methyl}$ (picrate, m.p. 193°), and n -butyl- (picrate, m.p. 239—240°), $\text{N}\cdot\text{benzyl-N}'\cdot n$ -butyl- (picrate, m.p. 171—172°), $\text{NNN}'\cdot\text{trimethyl}$ (picrate, m.p. 214°), and $\text{NN}\cdot\text{dimethyl-N}'\cdot n$ -butyl-guanidine (picrate, m.p. 118°), formed by way of the aldimine. R. S. C.

Formation of organo-metallic alkyl derivatives of aluminium during the polymerisation of ethylene. F. C. HALL and A. W. NASH (J. Inst. Petroleum Tech., 1937, 23, 679—687).— C_2H_4 with Al and AlCl_3 gives probably AlEtCl_2 , separated as a mol. compound with NaCl, with probably AlEt_3 and Al Et_2 chloride, b.p. 214—215°/750 mm., which does not polymerise C_2H_4 below 200°/48 atm., proving freedom from AlCl_3 , but at 250° forms Δ^2 -butene and even-C polymerides, presumably by Taylor and Jones' (A., 1930, 757) mechanism of free alkyl radicals.

F. R. G.

Pyrolysis of (A) phenylcyclohexane and tert -butylnaphthalene, (B) triphenylmethane. A. F. DOBRIANSKI and S. V. KATZMAN (J. Gen. Chem. Russ., 1937, 7, 1352—1354, 1355—1356).—(A) Phenylcyclohexane (I) is converted into $\text{CH}_2\cdot\text{CHPh}$, C_{10}H_8 , gaseous hydrocarbons, and H_2 , and $\text{C}_{10}\text{H}_7\cdot\text{Bu}'$ (II) into C_{10}H_8 , $(\text{C}_{10}\text{H}_7)_2$, and gaseous products, when heated at 600°. It is concluded that the pyrolysis of (I) involves rupture of the cyclohexane ring, as well as dissociation to Ph and cyclohexyl, whilst pyrolysis of (II) consists exclusively in elimination of Bu' .

(B) CHPh_3 yields C_6H_6 , CH_2Ph_2 , and H_2 when subjected to pyrolysis at 710° . R. T.

Oxidation of heptylbenzene and decahydronaphthalene in the liquid phase. N. I. TSCHERNOSHUKOV and S. E. KREIN (J. Appl. Chem. Russ., 1937, 10, 1435—1449).—Oxidation of heptylbenzene (I) by air ($78-124^\circ/10$ atm.) consists of the reactions (I) \rightarrow peroxides $\rightarrow \text{PhCHO} + \text{Bu}^n\text{CHO}$; $\text{PhCHO} \rightarrow \text{BzOH} \rightarrow \text{OH-acids} \rightarrow \text{lactones, esters, and resins}$; $\text{Bu}^n\text{CHO} \rightarrow \text{EtCO}_2\text{H, AcOH, HCO}_2\text{H, CO, and CO}_2$. The corresponding reactions with decahydronaphthalene (II) are: carboids \leftarrow carbenes \leftarrow asphaltenes \leftarrow tars \leftarrow condensation products \leftarrow (II) \rightarrow acids \rightarrow OH-acids \rightarrow asphaltic acids. R. T.

Chlorination of nitrobenzene in presence of ferric chloride. H. E. FIERZ-DAVID and F. R. STÄHELIN (Helv. Chem. Acta, 1937, 20, 1458—1461).—Chlorination of dry PhNO_2 by dry Cl_2 in presence of anhyd. FeCl_3 at 40° yields *m*-, *o*-, and *p*- $\text{C}_6\text{H}_4\text{ClNO}_2$ and 1:2:5- $\text{C}_6\text{H}_3\text{Cl(NO}_2)_2$. At higher temp. considerable amounts of C_6Cl_6 are derived from PhNO_2 , not from C_6H_6 . H. W.

Condensations by sodium. X. Side reactions occurring in Wurtz syntheses. Formation of iodobenzene. A. A. MORTON and F. FALLWELL, jun. (J. Amer. Chem. Soc., 1937, 59, 2387—2390; cf. A., 1937, II, 101).—Na amyl (I) and MeI give $\text{C}_{10}\text{H}_{22}$ (50%), CH_4 , and some C_2H_6 , but no unsaturated compounds. Other alkyl halides give varying yields of the dialkyl, $\text{C}_5\text{H}_{11}\text{R}$, always $<$ that of the hexoic acid obtained by CO_2 . The yield of $\text{C}_{10}\text{H}_{22}$ is also that of the acid. At -72° EtBr gives the same amount of C_7H_{16} , but more $\text{C}_{10}\text{H}_{22}$. NaPh and NaCH_2Ph with MeI give PhMe and PhEt, respectively, with no Ph_2 . Rapid addition of I to NaPh gives 6.3% of Ph_2 and 15% of PhI, but slow addition gives 12.5 and 1.6%, respectively; the PhI is thus an intermediate in the prep. of Ph_2 . Na_2 amylene and EtBr do not react, nor does (I) with CH_2Cl_2 or $(\text{CH}_2\text{Cl})_2$. In all reactions indefinite polymerides of high b.p. are also formed. R. S. C.

Decomposition of aromatic sulphonic acids by phosphoric acid. V. VESELY and T. STOJANOVA (Coll. Czech. Chem. Comm., 1937, 9, 465—469).—The temp. at which H_3PO_4 effects the removal of SO_3H from substituted benzene- and 1:2:3:4-tetrahydronaphthalene-sulphonic acids are recorded. The elimination is aided by alkyl and halogen groups, and inhibited by NO_2 -groups. J. D. R.

Action of lithium on $\alpha\alpha\alpha\alpha$ -pentaphenylpropylene. C. F. KOELSCH and R. H. ROSENWALD (J. Amer. Chem. Soc., 1937, 59, 2170—2171).— $\text{CPh}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ and LiPh (not MgPhBr) give $\alpha\alpha\alpha\alpha$ -pentaphenylpropanol, m.p. $139-140^\circ$, converted by SOCl_2 into $\alpha\alpha\alpha\alpha$ -pentaphenylpropylene (I), m.p. $132-133^\circ$, also obtained in poor yield with 1:1:3:3-tetraphenylhydrindene (II), m.p. $191-192^\circ$ (stable to KMnO_4), by 4% $\text{H}_2\text{SO}_4\text{-AcOH}$. With 4% $\text{H}_2\text{SO}_4\text{-AcOH}$ (I) gives (II), with CrO_3 , COPh_2 and $\text{CPh}_3\cdot\text{OH}$, and with Na-BuOH $\alpha\alpha\alpha\alpha$ -pentaphenylpropane, m.p. $158-159^\circ$. 40% Na-Hg reacts very slowly with (I), but Li in Et_2O gives a red solution, which with EtOH gives, *inter alia*, $(\text{CHPh}_2\cdot\text{CH})_2$ and CHPh_3 , and

with CO_2 affords $\text{CPh}_3\cdot\text{CO}_2\text{H}$ and $(\text{CH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H})_2$; fission into CPh_3 and $\text{CPh}_2\cdot\text{CH}$ thus occurs. 3-Phenyl-1-diphenylindene and Li in Et_2O give 9-phenyl-1:2:3:4-dibenzofluorene. R. S. C.

Dehydrogenation of hydroaromatic hydrocarbons with an alkyl disulphide. J. J. RITTER and (Miss) E. D. SHEARPE (J. Amer. Chem. Soc., 1937, 59, 2351—2352).—(*iso*- C_5H_{11}) $_2\text{S}_2$ with tetrahydronaphthalene or ionene at about 250° gives 70% of C_{10}H_8 or 32% of 1:6- $\text{C}_{10}\text{H}_6\text{Me}_2$, respectively. The latter dehydrogenation leads to 0.5 mol. of gas, containing 85% of CH_4 and a small amount of unsaturated compounds; the same reaction with S also leads to 0.5 mol. of CH_4 . R. S. C.

Photo-sensitive nitro-compounds. V. Nature of products of the photo-reaction of 1-nitronaphthalene-8-sulphonic acid. N. N. VOROSHOV and V. V. KOZLOV (J. Gen. Chem. Russ., 1937, 7, 1610—1613).—The ppt. forming when 5% aq. 1:8- $\text{NO}_2\text{-C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ (I) is exposed to sunlight (2—3 weeks) is 1'-nitro-1-amino-2-hydroxydinaphthylsulphone. The Mg salt of (I) yields similarly Mg 1:1'-azo-2-hydroxynaphthalene-8:8'-disulphonate, reduced by TiCl_3 to 1-aminocroceic acid. R. T.

Dehydration of derivatives of cyclopentanol. J. I. DENISENKO and A. D. NABER (Bull. Acad. Sci., U.R.S.S., 1937, Sér. Chim., 944—945).—1- γ -Phenylpropyl- and 1- β -phenylethyl-cyclopentanol are dehydrated normally by $\text{H}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$, but with anhyd. $\text{H}_2\text{C}_2\text{O}_4$ (2 parts) at $130-135^\circ$ give 1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. $283-284^\circ/744.5$ mm. (converted by Pt-C at 300° in CO_2 or H_2 into phenanthrene), and 1:2-cyclopentano-1:2:3:4-tetrahydronaphthalene, b.p. $266-267^\circ/739.2$ mm., respectively. R. S. C.

Reduction of alkali metals with polycyclic hydrocarbons. II. W. E. BACHMANN and L. H. PENCE (J. Amer. Chem. Soc., 1937, 59, 2339—2342; cf. A., 1937, II, 184).—Various benzantracenes with Na or Li in $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$ give the 9:10-disodio- (A) or 9:10-dilithio- (B) -9:10-dihydro-derivatives. The colour of (A) usually differs from that of (B) and the difference is ascribed to a difference in the mode of addition (*cis* or *trans*). Treatment of (A) or (B) with MeOH usually gives the same 9:10- H_2 -derivatives, which are dehydrogenated (S at $200-230^\circ$) to the parent hydrocarbons and oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$, AcOH) to the corresponding 9:10-anthraquinones. Treatment of (B) with CO_2 affords the corresponding dicarboxylic acids; (A) similarly give (usually) the monocarboxylic acids but variable results are noted. Thus, 1:2:3:4-dibenzanthracene (obtained in 56% yield from 9-*o*-toluoylphenanthrene and Zn dust at $400-420^\circ$) gives its 9:10- H_2 -derivative, m.p. $202-203^\circ$, and 9:10-dihydro-1:2:3:4-dibenzanthracene-9-carboxylic acid, m.p. $227.5-230^\circ$ (decomp.) (Me ester, m.p. $158-164^\circ$), and -9:10-dicarboxylic acid, m.p. $270-274^\circ$ (decomp.) (Me $_2$ ester, m.p. $236-238^\circ$). 6-Methyl-1:2:3:4-dibenzanthracene, m.p. $157.5-158^\circ$ [formed by pyrolysis of 9-(*m*-4-xyloyl)phenanthrene (from 2:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{MgBr}$ and 9-cyanophenanthrene)], is oxidised to the quinone, m.p. $187.5-188.5^\circ$, and.

affords its 9:10- H_2 -derivative, m.p. 207—209.5°. 1:2:6:7-Dibenzanthracene (from 3-*o*-toluoylphenanthrene and Zn dust at 400—420°) affords a H_2 -derivative, m.p. 157—160.5° [from (B)]; a mixture is obtained from (A)]. 1:2:3:4:5:6-Tribenzanthracene [obtained in 44% yield from 9-(2-methyl-1-naphthoyl)phenanthrene and Zn dust at 410°] yields the 9:10- H_2 -derivative, m.p. 281—283°. 5-Methyl-, m.p. 128—129.5°, and 5-phenyl-, m.p. 96—96.5°, -9:10-dihydro-1:2-benzanthracenes are prepared. 9:10-Dihydro-1:2-benzanthracene-9:10-dicarboxylic acid, m.p. 252° (decomp.) (Me_2 ester, m.p. 143.5—145°) [from (B)]; variable results with (A)], 9:10-dihydro-1:2:5:6-dibenzanthracene-9-carboxylic acid, m.p. 242—255° (decomp.) (Me ester, m.p. 174—175°) [usually obtained with (A)], and -9:10-dicarboxylic acid, m.p. 262—264° (decomp.) (Me_2 ester, m.p. 255—257°) [from (B)], and 11:14-dihydro-20-methylcholanthrene-carboxylic acid (Me ester, m.p. 178—179°) and -11:14-dicarboxylic acid, m.p. 242—246° (Me_2 ester, m.p. 205—208°) (for numbering see A., 1935, 1117), are described. H. B.

10-isoPropyl-1':2':3':4'-tetrahydro-1:2-benzanthracene. L. F. FIESER and E. B. HIRSCHBERG (J. Amer. Chem. Soc., 1937, 59, 2331—2335).—In one experiment high-pressure hydrogenation of 1- $C_{10}H_7 \cdot CO \cdot C_6H_4 \cdot CO_2H$ -*o* gave some *o*-5:6:7:8-tetrahydronaphthylmethylbenzoic acid (I), m.p. 166—166.5°, which is cyclised to 1':2':3':4'-tetrahydro-1:2-benz-10-anthranyl acetate, m.p. 116—118°, converted by $MgBu^+Br$ into 1':2':3':4'-tetrahydro-1:2-benz-10-anthrone (II), m.p. 181—182°. With $MgPr^+Br$ this gives 10-isopropyl-1':2':3':4'-tetrahydro-1:2-benzanthracene, m.p. 81.9—82.5° (picrate, m.p. 134.5—135°), identical with the by-product obtained starting from crude 1- $C_{10}H_7 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$ -*o* (Fieser *et al.*, A., 1937, II, 333). Tetrahydronaphthylamine, b.p. 279—279.3°/763 mm., gives (diazotisation, $CuBr \cdot Cu \cdot HBr$) 52% of 1-bromo-5:6:7:8-tetrahydronaphthalene, b.p. 135—140°/16 mm., the Mg derivative from which with *o*- $C_6H_4(CO)_2O$ affords *o*-5:6:7:8-tetrahydronaphthylbenzoic acid (III), m.p. 207—207.5°, reduced by $Zn \cdot NaOH$ to (I) and α -1-5':6':7':8'-tetrahydronaphthylphthalide, m.p. 123.5—124°, or, best, by $H_2 \cdot Cu$ chromite at 215°/2800 lb. to (I). Oxidation of (II) gives 1':2':3':4'-tetrahydro-1:2-benzanthraquinone, m.p. 157.5—158.5° (gives a red-orange vat). The so-called H_2 -compounds of Wilstätter *et al.* (A., 1921, i, 668) were (I) and (II).

R. S. C.

Cyclisation of 2-(β -1'-naphthylethyl)- Δ^2 -cyclopentenone. S. H. HARPER (J.C.S., 1937, 1859).—2-(β -1'-Naphthylethyl)- Δ^2 -cyclopentenone with P_2O_5 at 130° gives 1:2-cyclopentenophenanthrene.

E. G. B.

Dehydrogenation and dealkylation of *sec.* and *tert.* amines by sulphur. C. M. ROSSER and J. J. RUTTER (J. Amer. Chem. Soc., 1937, 59, 2179—2181).—Substituted anilines, $NPhR \cdot CHR'_2$, in which $R = H$, alkyl, or Ac , are converted by S at the b.p. or about 200—230° into anils, which usually react further with the H_2S or RHS evolved or condense. $NHPh \cdot CHPh_2$, b.p. 233°/20 mm., gives 65% of $NPh \cdot CPh_2$ with H_2S (90%) and a little NH_2Ph and $CSPH_2$.

B** (A., II.)

$NHPh \cdot CHPhEt$, b.p. 172°/9 mm., gives $NPh \cdot CPhEt$ (30%), H_2S (80%), NH_2Ph , and tars. *iso*Bornyl-*p*-dimethylaminoaniline, b.p. 171—173°/1 mm., gives 50% of camphoranil and 85% of H_2S . $NHPhPr^s$, b.p. 87—89°/13 mm., gives only traces of $COMe_2$. $NPhPr^sR$ ($R = Me$, b.p. 215—218°, Et , b.p. 223—225°/760 mm., 100—102°/13 mm., or Pr^s , b.p. 225—227°/760 mm., 98—100°/13 mm.) gives $NPh \cdot CMe_2$ (23%), b.p. 85—87°/13 mm., 199—202°/760 mm., $NHPhPr^s$ (35%), Pr^sSH (30%), and small amounts of mesityl oxide anil, NH_2Ph , and $Pr^s_2S_2$. *iso*Bornylacetanilide gives camphoranil (40%), $MeCS \cdot OH$ (10%), and H_2S (50%). $NHPhPr^s$ and $Pr^s_2S_2$ give Pr^sSH (20%) and $NPh \cdot CMe_2$. *iso*Bornylaniline is similarly dehydrogenated by $(C_5H_9)_2S_2$. Fission of $NPh \cdot CPh_2$ by H_2S at 220° into NH_2Ph and $CSPH_2$ is demonstrated. R. S. C.

Evidence of restricted rotation about the $N \cdot C$ bond in 2:6-disubstituted acetanilides. L. HUNTER and H. O. CHAPLIN (Nature, 1937, 140, 896).—In the anilides, certain *o*-substituents prevent association. These are invariably H -acceptor groups such as NO_2 , NN , and CO_2Et . In such compounds the H responsible for association is concerned in chelation and is not available for association. Substitution in the second *o*-position restores the tendency to associate and prevents chelate formation. This is interpreted as evidence of restricted rotation about the N -nuclear single linking in 2:6-disubstituted acetanilides. L. S. T.

Bromination of 4-acetamidodiphenyl. F. H. CASE and H. A. SLOVITER (J. Amer. Chem. Soc., 1937, 59, 2381—2382).—The product (I), m.p. 145°, obtained by bromination of *p*- $C_6H_4Ph \cdot NHAc$ (II) is a mixture of 3-bromo- (III) and 3:4-dibromo-4-acetamidodiphenyl (IV), being resolved into 1:3:4- $C_6H_3PhBr \cdot NH_2$ and 3:4-dibromo-4-aminodiphenyl, m.p. 107—108°, by hydrolysis and distillation. Br (2 mols.) and (I) in $AcOH$ give 4- $C_6H_4Br \cdot C_6H_4 \cdot NHAc$ -4, 3:5:4'-tribromo-4-aminodiphenyl, and a little (I), but in presence of $NaOAc$ mainly (IV) and some (I). Diazotised 4:3:1- $NO_2 \cdot C_6H_3Br \cdot NH_2$ (prep. from *m*- $C_6H_4Br \cdot NHAc$) gives with C_6H_6 3-bromo-4-nitrodiphenyl, b.p. 252—254°/7 mm., whence (III) is obtained by reduction ($SnCl_2$) and acetylation.

R. S. C.

Diphenyl series. X. Bromination of some 2:4'-diphenyl derivatives. V. BELLAVITA (Gazzetta, 1937, 67, 574—579).—4-Nitro-2:4'-diaminodiphenyl (A., 1932, 1025) with Br gives its 3':5'- Br_2 -derivative, m.p. 197° (Ac_2 derivative, m.p. 188—190°), of which the structure is established by conversion (diazotisation and H_2PO_2) into 3':5'-dibromo-4-nitrodiphenyl (I), m.p. 160°, identical with the product derived from 4'-nitro-2-aminodiphenyl. The substances previously regarded (A., 1937, II, 187) as 3:4-dibromo-4'-nitro-2-amino-, 3:4-dibromo-2:4'-diamino-, and 3:4-dibromo-4'-nitro-diphenyl are now renamed as 3:5-dibromo-4'-nitro-2-amino- and 3:5-dibromo-2:4'-diamino-diphenyl, and (I). The reduction product of (I), "3:4-dibromo-4'-aminodiphenyl," is renamed 3':5'-dibromo-4-aminodiphenyl; when diazotised and reduced it gives 3:5-dibromodiphenyl,

new m.p. 42° (cf. A., 1926, 513), oxidised to 3:5:1- $C_6H_3Br_2 \cdot CO_2H$. E. W. W.

Plano-radiate compounds. V. Amides from hexa-aminobenzene. H. J. BACKER and S. J. VAN DER BAAN (Rec. trav. chim., 1937, 56, 1175—1186).— $C_6(NH_2)_6$ (I) is methylated (Me_3SO_4 -KOH) to hexa(dimethylamino)benzene, m.p. 236° (trihydrochloride). When heated with the appropriate acid anhydride, or acid chloride and pyridine, $C_6(NH_2)_6$ yields hexa-amides $C_6(NH \cdot CO \cdot R)_6$. Thus are obtained hexa-acet-, m.p. 358° (decomp.), -propion-, m.p. 360° (decomp.), -n-butyro-, m.p. 360° (decomp.), -isobutyro-, m.p. 384° (decomp.), -n-valer-, m.p. 335° (decomp.), -isovaler-, m.p. 366—367°, - α -methyl-n-butyro-, m.p. 345° (decomp.), - α -dimethylpropion-, decomp. 367°, -n-hepto-, m.p. 329° (decomp.), -phenylacet-, m.p. 340° (decomp.), -benz-, m.p. 405° (decomp.), -p-tolu-, m.p. <400° and -p-chlorobenzamidobenzene, m.p. <400°. The m.p. are discussed and some crystallographic data given. J. D. R.

Manufacture of [higher] alkylanilinemonosulphonic acids.—See B., 1937, 1175.

Preparation of ar-tetrahydronaphthylthio-ureas.—See B., 1937, 1175.

Manufacture and application of [higher] quaternary ammonium salts.—See B., 1937, 1177.

Manufacture of cyclic aminosulphonic acid amides.—See B., 1937, 1269.

Action of nitrous acid on amines. J. C. EARL and N. G. HILLS (J. Proc. Roy. Soc. New South Wales, 1937, 70, 322—326; cf. A., 1933, 498, 705).—Measurements of vol. and conductivity during the reaction of NH_2Ph and of $NHPhMe$ with $NaNO_2$ and HCl in MeOH indicate the formation of an intermediate substance, and an increase in p_H towards the end of the reaction. A. Lr.

Diazo-compounds. I. Diazotisation of amines in presence of stannous salts. V. V. KOZLOV (J. Gen. Chem. Russ., 1937, 7, 1635—1644).—Amines which are under the ordinary conditions resistant to diazotisation (aminophenols) are readily diazotised in acid or neutral solution in presence of $SnCl_2$, which not only catalyses the reaction but also stabilises the diazo-product. R. T.

Migration of alkyl radicals. Scission of a tertiary octyl group. R. A. SMITH and C. J. RODDEN (J. Amer. Chem. Soc., 1937, 59, 2353).— $p-CH_2Bu^{\gamma} \cdot CMe_2 \cdot C_6H_4 \cdot OH$ (1 mol.), $PhOH$ (1 mol.), and technical $AlCl_3$ (2.33 mols.) at 100° give $p-C_6H_4Bu^{\gamma} \cdot OH$, also obtained in 67% yield from diisobutylene, $PhOH$, and $AlCl_3$ at 100°. R. S. C.

Derivatives of 3-n-propylphenol. S. G. COUSIN and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1937, 70, 413—427; cf. Ciamician and Silber, A., 1890, 965).—*m-n*-Propylphenol (I), prepared by treating a hot mixture of Na and isosafrole with hot EtOH, acidifying the aq. layer, and fractionating the phenols, gives benzyl, b.p. 184—185°/12 mm., *p*-nitrobenzyl, m.p. 43°, and allyl, b.p. 125—126°/13 mm., ethers. The last is isomerised by heat (230°) to 3-n-propyl-6-allylphenol, b.p. 142—144°/16 mm., which with $CH_2Cl \cdot CO_2H$ and NaOH (Koelsch, A.,

1931, 345) yields 3-n-propyl-6-allylphenoxycetic acid, m.p. 47°, and when boiled with KOH in partial vac. yields a substance, b.p. 137—138°/16 mm. (possibly 3-propyl-6-propenylphenol), which neither reacts with $CH_2Cl \cdot CO_2H$, nor is reduced by Na + EtOH. The acetate, b.p. 238—240°, of (I) when boiled with Ac_2O and a little conc. H_2SO_4 for 2 hr. yields (?) 4-acetyl-3-n-propylphenol, b.p. 121—123°/18 mm. (corresponding aryloxyacetic acid, m.p. 73°). Other derivatives of (I) are the benzoate, m.p. 114°, 3:5-dinitrobenzoate, m.p. 77°, aryloxyacetic acid, m.p. 70°, Et 3-n-propylphenyl carbonate, b.p. 140—142°/14 mm. ($NaOH$ and $ClCO_2Et$), and the 2:4:6-(NO_2)₃-[conc. H_2SO_4 and HNO_3 (d 1.42) at 100°], m.p. 65—66°, and - Br_3 -compound (Br in glacial AcOH), m.p. 85°. 3-n-Propylanisole reacts with $Bu^{\gamma}Cl$ and $AlCl_3$ giving 3-n-propyl-6-tert.-butylanisole, b.p. 129—132°/15 mm., nitrated (fuming HNO_3 in Ac_2O) to the 2:4-(NO_2)₂-compound (sweet musk odour), m.p. 41°. Heating (I) at 180° for 5 hr. with $ZnCl_2$ and a fatty acid yields the 6-acyl-3-n-propylphenol: acetyl, b.p. 128—131°/16 mm. [aryloxyacetic acid, m.p. 52°, and oxime ($NH_2OH \cdot HCl$ and $BaCO_3$ in boiling NaOH), m.p. 74°, which in AcOH or EtOH gives a ppt. with $Cu(OAc)_2$, and is therefore the oxime of an o-acylphenol]; propionyl, b.p. 124—125°/13 mm. (aryloxyacetic acid, m.p. 62°; semicarbazone, m.p. 132°); n-butyryl, b.p. 130—132°/19 mm. (aryloxyacetic acid, m.p. 67°; semicarbazone, m.p. 175°), together with a small amount of phenolic substance, b.p. 151—153°/19 mm.; n-valeryl, b.p. 127—129°/18 mm. (aryloxyacetic acid, m.p. 69°). These ketones could not be esterified, but are reduced (Clemmensen) to 3-n-propyl-6-alkylphenols, the phenol coeff. of which for *B. typhosus* is >1: Et, b.p. 126—127°/15 mm. [*Me* ether, b.p. 112—114°/26 mm., oxidised ($KMnO_4$) to $m-CO_2H \cdot C_6H_4 \cdot OMe$ and another acid, m.p. >250°]; Pr^a , b.p. 131—132°/15 mm.; Bu^a , b.p. 137—139°/30 mm.; n-amyl, b.p. 127—128°/14 mm. These yield aryloxyacetic acids of m.p.: Et 75°, Pr^a 69°, Bu^a 67°, n-amyl 64°. Mercuration of (I) with excess of $Hg(OAc)_2$ in EtOH-AcOH gives a product, m.p. 220—225°. (I) couples with diazotised *p*-toluidine or *m*-nitroaniline giving dyes, m.p. 125—127° and 139—142°, respectively, and with diazotised NH_2Ph , 2:4- $C_6H_3Cl_2 \cdot NH_2$, or $\beta-C_{10}H_7 \cdot NH_2$, giving brown oils. A. Lr.

Polymerides of methylchavicol. J. M. VAN DER ZANDEN (Proc. K. Akad. Wetensch. Amsterdam, 1937, 40, 706—709).—Prolonged (200 hr.) heating of methylchavicol at 250° under pressure affords an oily volatile product and α -di-*p*-anisyl- Δ^a -hexene (I), m.p. 93°. Oxidation ($KMnO_4$ - $COMe_2$) of (I) affords *p*-anisic acid and 8-*p*-anisylvaleric acid (II), m.p. 114—114.5° (lit., 113°), which is oxidised to γ -*p*-anisoylbutyric acid, m.p. 140—140.5° (lit., 138°) [*p*-nitro-, m.p. 198—200°, and 2:4-dinitro-phenylhydrazones, m.p. 142.5°; the oxime (III), m.p. 97—97.5°, suffers rearrangement and hydrolysis with H_2SO_4 to give glutaric acid (IV)], synthesised from $PhOMe$, (IV), and $AlCl_3$. (I) with H_2 -Pd affords α -di-*p*-anisylhexane. (III) with PCl_5 in Et_2O affords an imide, m.p. 172—172.5° [synthesised from (IV) and *p*-anisidine], converted by 1 equiv. of

KOH into an acid, $C_{12}H_{15}O_4N$, m.p. 147—148°, hydrolysed (conc. HCl) to (IV) and *p*-anisidine. *p*-Anisaldehyde with EtOAc in presence of Na affords Et *p*-methoxycinnamate, reduced (Na dissolving in EtOH) to *p*-anisylpropyl alcohol, m.p. 25—26°, the bromide of which with $CHNa(CO_2Et)_2$ affords a compound which when hydrolysed and decarboxylated gives (II). J. L. D.

Preparation of β -dinaphthol by Dianino's reaction. I. GRATSCHEV (Prom. Org. Chim., 1937, 4, 298—299).— β - $C_{10}H_7\cdot OH$ is oxidised to 2:2'-dihydroxy-1:1'-dinaphthyl by $FeCl_3$ in presence of NaOAc. R. T.

Action of hydroxylamine on certain naphthalene derivatives. S. V. BOGDANOV and I. I. LEVKOEV (J. Gen. Chem. Russ., 1937, 7, 1539—1542).—1-Amino-2-naphthol-6-, -7-, or -8-sulphonic acid and NH_2OH in boiling 1% HCl yield NH_4 2-nitroso- α -naphthol-6-, -7-, or -8-sulphonate. R. T.

Reaction of *o*-chlorothiolenitrobenzene chloride with potassium hydrogen sulphide. G. DOUGHERTY and O. HAAS (J. Amer. Chem. Soc., 1937, 59, 2469—2470).— o - $NO_2\cdot C_6H_4\cdot SCl$ and KHS give KCl, H_2S , and $(NO_2\cdot C_6H_4)_2S_2$, probably by way of $NO_2\cdot C_6H_4\cdot S\cdot SH$, which decomposes to the disulphide and H_2S . Interaction of C_6H_6 , $AlCl_3$, and S is thus probably: $C_6H_6 + S_2 (+AlCl_3) \rightarrow PhS\cdot SH$; $2PhS\cdot SH \rightarrow Ph_2S_2 + H_2S + S$; $Ph_2S_2 + S (+AlCl_3) \rightarrow C_6H_4\langle \begin{smallmatrix} S \\ S \end{smallmatrix} \rangle C_6H_4 + H_2S$. R. S. C.

Some additive reactions of nitrostyrenes. C. MUSANTE (Gazzetta, 1937, 67, 579—588).— β -Nitro- α -*p*-anisylethylene (I) (A., 1910, i, 106) and $N_2H_4\cdot H_2O$ in EtOH yield anisaldazine and $MeNO_2$. $CHPh\cdot CH\cdot NO_2$ with $N_2H_4\cdot H_2O$, yields benzaldazine, and, with $NHPh\cdot NH_2$, $NO_2\cdot CH_2\cdot CHPh\cdot NH\cdot NHPh$ (II) (A., 1927, 761). With $NHPh\cdot NH_2$, (I) gives β -nitro- α -phenylhydrazino- α -*p*-anisylethane (III), m.p. 112°. β -Nitro- α -3:4-dimethoxyphenylethylene and $NHPh\cdot NH_2$ yield β -nitro- α -phenylhydrazino- α -3:4-dimethoxyphenylethane (IV), m.p. 112—113°. When (II), (III), and (IV) are heated, they readily yield $CHR\cdot N\cdot NHPh$ and $MeNO_2$. β -Nitro- α -phenylhydrazino-3:4-methylenedioxyphenylethane, m.p. 121°, obtained similarly, gives only a poor yield of the phenylhydrazone. β -Nitro- α -*p*-nitrophenylethylene and $NHPh\cdot NH_2$ yield β -nitro- α -phenylhydrazino- α -*p*-nitrophenylethane, m.p. 123° (decomp. to the phenylhydrazone), which is oxidised by SeO_2 in EtOH at the b.p. to ω -dinitroacetophenonephenylhydrazone, m.p. 141—142° (decomp.), also obtained from the ketone. β -Bromo- β -nitro- α -*p*-anisylethylene, m.p. 67°, from the dibromide of (I) (cf. A., 1935, 616), with $NHPh\cdot NH_2$, gives only anisaldehydephenylhydrazone and $CH_2Br\cdot NO_2$. Et ω -dinitrocinnamate also yields *p*- $NO_2\cdot C_6H_4\cdot CH\cdot N\cdot NHPh$, and β -nitro- α -4-hydroxy-3-methoxyphenylethylene behaves similarly. E. W. W.

Condensation products of 3:5-dibromo-2-hydroxybenzyl bromide with phenols. Their germicidal power. W. C. HARDEN and J. H. BREWER (J. Amer. Chem. Soc., 1937, 59, 2379—2380).—2:3:5- $OH\cdot C_6H_2Br_2\cdot CH_2Br$ and the appro-

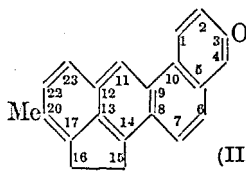
priate phenol with Zn or Na_2CO_3 in PhMe or in aq. alkali give 3:5-dibromo-2:4'-dihydroxy-, m.p. 172—174°, 3:5:3':5'-tetrabromo-2:4'-dihydroxy-, m.p. 195—197°, 3:5-dibromo-3':5'-di-iodo-2:4'-dihydroxy-, m.p. 199—200°, 3:5-dibromo-2:2':4'-trihydroxy-, m.p. 198—199°, 3:5:3':5'-tetrabromo-2:2':4'-trihydroxy-, m.p. 213—214°, 3:5-dibromo-2:4'-dihydroxy-2', m.p. 135—137°, and -3'-methyl-, m.p. 154—155°, 3:5:3':5'-tetrabromo-2:4'-dihydroxy-2', m.p. 157—158°, and -3'-methyl-diphenylmethane, m.p. 190—192°. The sol. Na salts of these products are fairly potent germicides. R. S. C.

Glucosides related to carcinogenic hydrocarbons. J. W. COOK and C. G. M. DE WORMS (J.C.S., 1937, 1825—1828).—An attempt to synthesise H_2O -sol. carcinogenic compounds. 6-Methoxy-1-naphtho-nitrile [improved prep. using $Ni(CN)_2$] and 4-methyl-hydrindyl-7-lithium (from the 7-Br-compound) give, after hydrolysis of the ketimine, 7-(6'-methoxy-1'-naphthoyl)-4-methylhydrindene, m.p. 86—87°, b.p. 245—250°/1 mm., which when heated at 405° and distilled (240—245°/0.3 mm.) yields 3-methoxy- (I), m.p. 165—166.5° (corr.), demethylated (HBr-AcOH) to the Ac. derivative, m.p. 191—192° (corr.), of 3-hydroxy-20-methylcholanthrene (II), m.p. 218.5—220° (corr.). With O-tetra-acetyl- α -glucosidyl bromide this yields 3-O-tetra-acetyl- β -glucosidoxy-20-methylcholanthrene, m.p. 210—211°, which is, however, deacetylated to an amorphous product, insol. in H_2O . Similarly 4'-hydroxy- (III) yields 4'-O-tetra-acetyl- β -glucosidoxy-3:4-benzpyrene, m.p. 184—185°, which is deacetylated to a glucoside, m.p. 270—273°, again amorphous and insol. Further, (I), (II), and (III) and its Me ether are devoid of carcinogenic activity (cf. A., 1937, III, 379). E. W. W.

Plano-radiate compounds. IV. Esters of hexahydroxybenzene. H. J. BACKER and S. J. VAN DER BAAN (Rec. trav. chim., 1937, 56, 1161—1174; cf. A., 1936, 1100).—The following esters of hexahydroxybenzene, $C_6(O\cdot COR)_6$, are obtained by fusing it with the appropriate acid anhydride, the Na salt of the acid, and a little Zn dust to avoid oxidation. Thus are obtained the acetate, m.p. 222° (decomp.); propionate, m.p. 137°; n-butyrate, m.p. 135°; isobutyrate, m.p. 157°; n-valerate, m.p. 109°; isovalerate, m.p. 167.5°; α -methyl-n-butyrate, m.p. 115.5°; pivalate (I), m.p. 316°; n-heptate, m.p. 85.5°; n-undecate, m.p. 89.5°. The following are prepared from the phenol and the appropriate acid chloride in presence of C_5H_5N : phenylacetate, m.p. 185.5°; benzoate, m.p. 313° (decomp.); p-chlorobenzoate, m.p. 328° (decomp.); p-toluate, m.p. 333° (decomp.). In the prep. of (I), hexahydroxybenzene pentapivalate, m.p. 180.5°, is also formed. Crystallographic measurements of several products are given, and the structures and m.p. are discussed. J. D. R.

Oxidation of phenols by ozone.—See A., I, 37.

Furfurylidene- and benzylidene-phenol systems and their fusion diagrams.—See A., I, 13.



Manufacture of hydroxysulphonic acids of [aromatic] hydrocarbons of high mol. wt.—See B., 1937, 1176.

Manufacture of diseek-alkyl polyhydric phenols.—See B., 1937, 1176.

Dehydration of homologues of cyclopentanol. I. J. I. DENISENKO and V. M. KOTELNIKOVA (J. Gen. Chem. Russ., 1937, 7, 1357—1359).—1- γ -Phenylpropylcyclopentanol yields

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene when heated at 130—135° with anhyd. $H_2C_2O_4$.

R. T.
Configurative relations of cyclohexylethyl- and ethylhexyl-carbinol. G. OVAKIMIAN, S. MAR-DASHEV, and P. A. LEVENE (Biochem. Z., 1937, 293, 410—414).—In these and previous experiments (A., 1932, 1027), Et lactate and α -hydroxybutyrate, structurally related, have been converted (Grignard) into cyclohexyl-methyl- (I) and -ethyl-carbinol (II), which have rotations of opposite sign. Correlation of (I) with methylhexylcarbinol (*loc. cit.*) establishes that of (II) with ethylhexylcarbinol. Et d-(-)- α -hydroxybutyrate (III), b.p. 114—118°/150 mm., $[\alpha]_D^{20}$ -5.03° (from Ba d-(-)- α -hydroxybutyrate, $[\alpha]_D^{20}$ -6.63° in H_2O , of which the acid is obtained by treating d-(+)- α -aminobutyrate with $NaNO_2-H_2SO_4$), is structurally correlated with (-)-cyclohexylethylcarbinol (IV) (*loc. cit.*) by the following steps. With MeI-Ag₂O, (III) yields Et d-(-)- α -methoxybutyrate, b.p. 108—110°/150 mm., α_D^{20} -42.77°, which with MgBr \cdot [CH₂]₅·MgBr gives (-)-1- α -methoxypropylcyclohexanol, b.p. 110—115°/13 mm., $[\alpha]_D^{20}$ -5.81°. This with Na, followed by CS₂ and MeI, forms a CS \cdot SH compound, decomposed on distillation (170—180°) to (-)-1- α -methoxypropyl- Δ^1 -cyclohexene, b.p. 173—175°, $[\alpha]_D^{20}$ -4.62°, reduced (Adams) to (-)- α -methoxypropylcyclohexane, b.p. 187°, $[\alpha]_D^{20}$ -7.28°, which is also obtained by methylating (IV). E. W. W.

α - β -Ethoxyethylphenylcarbamide. E. WERTHEIM (J. Amer. Chem. Soc., 1937, 59, 2472—2473).—CH₂Ph·CH₂·ONa and EtBr give β -phenylethyl Et ether, b.p. 198—199°, converted by AcNO₂-Ac₂O at -5° into the α , b.p. 129—134°/6 mm., with a little of the p -NO₂-compound, b.p. 139—143°/6 mm. (give o - and p -NO₂·C₆H₄·CO₂H, respectively). Sn-HCl gives the o -NH₂-ether, b.p. 115—120°/4 mm., which with NH₂·CO·NH·NO₂ gives α - β -ethoxyethylphenylcarbamide, m.p. 155—156° (very faint sweet taste). R. S. C.

Synthesis of acetylenic alcohols and asymmetrical acetylene glycols. V. K. TETERIN and A. P. IVANOV (J. Gen. Chem. Russ., 1937, 7, 1629—1631).—MgEtBr and CHMe·CH·CH(OH)·C \equiv CH in Et₂O and CPh₃ yield $\alpha\alpha$ -diphenylhept- ϵ -en- β -yn- $\alpha\delta$ -diol, m.p. 124°. (BrMgC \equiv)₂ and CPh₃ give $\alpha\alpha$ -diphenylprop- β -yn- α -ol, m.p. 44—45°. R. T.

Preparation of some alkylated dihydrocholesterols (3-alkylcholestanols). C. C. BOLT and H. J. BACKER (Rec. trav. chim., 1937, 56, 1139—1141).—From cholestanone and the appropriate alkyl halide, the following are obtained by the Grignard reaction: 3-methyl-, m.p. 129—130°, 3-isopropyl-, m.p. 116—117°, 3-tert.-butyl-, m.p. 116—116.5°, $[\alpha]_D^{20}$

+26.7° in Et₂O, 3-cyclohexyl-, m.p. 162—163°, 3-phenyl-, m.p. 165—165.5°, 3- α -naphthyl-, m.p. 196—196.5°, $[\alpha]_D^{20}$ +27.2° in Et₂O, and 3- β -naphthyl-cholestan-3-ol, m.p. 232—233°, $[\alpha]_D^{20}$ +30.9° in Et₂O.

J. D. R.

Sterols. XXI. Lanosterol and agnosterol. R. E. MARKER and E. L. WITTLE (J. Amer. Chem. Soc., 1937, 59, 2289—2290).— α -Dihydroagnosterol (I) and Cu at 250°/2 mm. give α -dihydroagnostenone, m.p. 130° (2:4-dinitrophenylhydrazones, m.p. 224°), which with Na-Pr⁸OH gives (I), and with Al(OPr⁸)₃ gives a mixture of (I) and epi- α -dihydroagnosterol, m.p. 130° (acetate, m.p. 160°; converted into the ketone by Cu), separated by way of the acetates. α -Dihydrolanostenone and Al(OPr⁸)₃ give similarly epi- α -dihydrolanosterol, m.p. 139° (acetate, m.p. 167.5°), reconverted into the ketone by Cu. The above reactions and the fact that the alcohols give no digitonides confirm the relationship and triterpenoid nature of the sterols. R. S. C.

Sterols. XXII. Pregnanediols and pregnanones. R. E. MARKER, O. KAMM, E. L. WITTLE, T. S. OAKWOOD, E. J. LAWSON, and J. P. LAUCIUS. XXIII. Pregnanediols in pregnancy urine of mares. R. E. MARKER, O. KAMM, H. M. CROOKS, T. S. OAKWOOD, E. J. LAWSON, and E. L. WITTLE (J. Amer. Chem. Soc., 1937, 59, 2291—2296, 2297—2298).—XXII. The four missing pregnanediols are synthesised. The diols related at C₍₂₀₎ to pregnanediol and allopregnanediol are termed α -forms, their epimerides being termed β -forms. Partial hydrolysis of the diacetates always gives the 20-acetates. Na in boiling xylene does not affect the configuration at C₍₂₀₎ and gives mainly the epimeride in which the OH attached to C₍₂₀₎ is *trans* relative to the H attached to C₍₅₎. Partial hydrolysis of allopregnane- $\alpha\alpha$ -diol diacetate, followed by oxidation and hydrolysis, gives allopregnane-20(α)-ol-3-one, m.p. 128° [semicarbazone, m.p. 245° (decomp.); acetate, m.p. 117°], hydrogenated (PtO₂) in AcOH at 30°/3 atm. to a mixture yielding allopregnane-3(β):20(α)-diol (II), m.p. 218° (diacetate, m.p. 168°). 20(α)-Acetoxypregnane-3-one (modified prep. from the diol diacetate) is hydrogenated (Pt) in AcOH containing a little HBr to 20(α)-acetoxypregnane-3(β)-ol, m.p. 147.5°, which affords pregnane-3(β):20(α)-diol, m.p. 182° (diacetate, m.p. 141°). Pregnane-3(β):20(β)-diol diacetate affords pregnane-20(β)-ol-3-one, m.p. 172° [semicarbazone, m.p. 245° (decomp.)]. allopregnane-3(α):20(α)-diol and Na in xylene give mainly (II); pregnane-3(α):20(α)- and -3(α):20(β)-diol give similarly mainly natural pregnane-3(α):20(α)- and -3(α):20(β)-diol, m.p. 231° (diacetate, m.p. 110°), respectively.

XXIII. By collecting the part of the carbinol fraction of pregnant mare's urine extract subliming at 150—210°/high vac., acetylating, and hydrolysing, a small amount of pregnanediol (III) is obtained. Oxidation of the non-phenolic portion, with or without hydrocarbons, gives a mixture of pregnane- (IV) and allopregnane-dione (V), isolated as sparingly sol. disemicarbazones, that of m.p. >325° of (V) being separable from that of m.p. 257° (decomp.) of (IV) by virtue of its still lower solubility. The yield of

diones indicates that mare's urine contains as much (III) as does human pregnancy urine and that progesterone may be the corpus luteum hormone in the former urine. R. S. C.

Constituents of plant seedlings. II. Neotocopherol, a constituent of wheat-germ oil and other constituents of the oil. P. KARRER, H. SALOMON, and H. FRITZSCHE (Helv. Chim. Acta, 1937, 20, 1422—1426; cf. A., 1937, II, 242).— α -Tritisterol (I), present in larger proportion in rice-germ oil than in wheat-germ oil, is a sec. alcohol oxidised by CrO_3 or $\text{Al}(\text{OEt})_3$ to the ketone, $\text{C}_{30}\text{H}_{48}\text{O}$, m.p. 103° (oxime, m.p. 184°). It is hydrogenated (PtO_2) to dihydro- α -tritisterol, m.p. 131° . It gives a cryst. dibromide which gives a yellow colour with $\text{C}(\text{NO}_2)_4$ so that (I) possibly contains a second, difficultly recognisable double linking. A further component of wheat-germ oil is triticol (II), $\text{C}_{26}\text{H}_{39}\text{OH}$ or, possibly, $\text{C}_{19}\text{H}_{37}\text{OH}$; it is a singly unsaturated aliphatic alcohol which contains three or four CMe groups and is characterised by a cryst. allophanate, $\text{C}_{22}\text{H}_{42}\text{O}_3\text{N}_2$ or $\text{C}_{21}\text{H}_{40}\text{O}_3\text{N}_2$, m.p. 74° . (II) appears to be isomeric with or closely related to phytol. Vitamin-E action is absent. A third component is neotocopherol (III), $\text{C}_{29}\text{H}_{50}\text{O}_2$ or $\text{C}_{28}\text{H}_{48}\text{O}_2$ [allophanate (IV), $\text{C}_{31}\text{H}_{52}\text{O}_4\text{N}_2$ or $\text{C}_{30}\text{H}_{50}\text{O}_4\text{N}_2$, m.p. 143 — 144° , $[\alpha]_{537}^{25} +6.7^\circ$ in CHCl_3], which strongly reduces boiling AgNO_3 and contains 1 OH (Zerevitinov). Attempts to hydrogenate (PtO_2) (III) or (IV) at atm. pressure were unsuccessful but the presence of double linkings is indicated by the intense, brown-yellow colour with $\text{C}(\text{NO}_2)_4$ and confirmed by the absorption spectrum, which closely resembles those of β - and δ -tocopherol but differs markedly from that of duroquinol. Several CMe groups are present in (III). H. W.

Syntheses in the camphane series. IV. Direct synthesis of dihydroisolauroic acid and isolauroic acid. P. C. GUHA and K. S. SUBRAMANIAN (Ber., 1937, 70, [B], 2228—2232).— $\text{CMe}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, $\text{CO}_2\text{Et}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, and Zn give a poor yield of $\text{Et}_2\beta$ -hydroxy- β' -carbethoxy- $\alpha\alpha\beta$ -trimethyladipate, converted by PBr_3 in anhyd. CHCl_3 at room temp. into $\text{Et}_2\beta'$ -carbethoxy- $\alpha\alpha\beta$ -trimethyl-s-dihydromuconate (I), b.p. 155 — $162^\circ/5$ mm., which is hydrolysed by $\text{KOH}\cdot\text{EtOH}$ to β' -carboxy- $\alpha\alpha\beta$ -trimethyl-s-dihydromuconic acid, m.p. 239 — 240° [anilide-anil, $\text{C}_{22}\text{H}_{22}\text{O}_3\text{N}_2$, m.p. 212° ; trianilide, m.p. 235° (decomp.)], converted into the anil when heated at 200° . β -Hydroxy- β' -carboxy- $\alpha\alpha\beta$ -trimethyladipic acid has m.p. 165 — 166° . Treatment of (I) with Na wire in C_6H_6 leads to Et_2 1:1:2-trimethyl- Δ^2 -cyclopenten-5-one-3:4-dicarboxylate (II), b.p. 125 — $128^\circ/3$ mm., and an uninvestigated substance, m.p. 127 — 128° . (II) is converted with difficulty by boiling dil. HCl , readily by boiling $\text{KOH}\cdot\text{EtOH}$, into 1:1:2-trimethyl- Δ^2 -cyclopenten-5-one-3-carboxylic acid (ketoisolauroic acid), m.p. 186 — 187° [oxime, m.p. 139 — 140° ; semicarbazone, m.p. 225° (decomp.)], which is reduced by Zn-Hg and boiling conc. HCl to dihydroisolauroic acid, b.p. 110 — $115^\circ/20$ mm. This is transformed by Br and red P into α -bromodihydroisolauroic acid, m.p. 124 — 125° , which with KOH —

EtOH gives isolauroic acid [1:1:2-trimethyl- Δ^2 -cyclopenten-3-carboxylic acid], m.p. 133 — 134° .

H. W.

2-Chloro-4:5-dinitrobenzoic acid. H. GOLDSTEIN and A. STUDER (Helv. Chim. Acta, 1937, 20, 1407—1412).—4:2- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{CO}_2\text{H}$ is converted by HNO_3 (d 1.52) and conc. H_2SO_4 at room temp. and then at 100° into 2-chloro-4:5-dinitrobenzoic acid (I), m.p. 165 (corr.). The constitution of (I) follows from its conversion by boiling 2N-NaOH into 2-chloro-5-nitro-4-hydroxybenzoic acid, by conc. NH_3 at room temp. into 2-chloro-5-nitro-4-aminobenzoic acid, m.p. 267° (corr.) [Ac derivative, m.p. 198° (corr.)], whence 5:2- $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{Cl}\cdot\text{CO}_2\text{H}$, and by $\text{NH}_3\cdot\text{EtOH}$ at $150^\circ/20$ atm. into 4:1:3- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2$. (I) is converted by $\text{KOH}\cdot\text{MeOH}$ at 50° into 2-chloro-5-nitro-4-methoxybenzoic acid, m.p. 235° (corr.) (K salt), reduced ($\text{SnCl}_2\cdot\text{HCl}$) to 2-chloro-5-amino-4-methoxybenzoic acid [hydrochloride; Ac derivative, m.p. 251° (corr.)]. (I) is transformed by NH_2Ph and K_2SO_3 at 100° into 2-chloro-5-nitro-4-anilinobenzoic acid, m.p. 254° (corr.), and by boiling NH_2Ph containing K_2CO_3 and a little Cu powder into 5-nitro-2:4-dianilinobenzoic acid, m.p. 240° (corr.; decomp.), accompanied by a little 4:4'-dinitro-5:5'-dianilindiphenyl-2:2'-dicarboxylic acid, m.p. 256° (corr.). H. W.

Dialkylaminoalkyl esters of p-aminobenzoic acid. W. B. BURNETT, R. L. JENKINS, C. H. PEET, E. E. DREGER, and R. ADAMS (J. Amer. Chem. Soc., 1937, 59, 2248—2252).—For esters, $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot[\text{CH}_2]_n\cdot\text{NR}_2$ ($n = 2$ or 3), $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NR}_2$, and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NET}_2$, toxicity increases as does the size of R (alkyl), but the anaesthetic value increases more rapidly. Increase of n to 4 or 5 increases the toxicity and, less so, the anaesthetic properties. Branching in R lowers the toxicity and anaesthetic power. The following are prepared from NHR_2 and $\text{OH}\cdot[\text{CH}_2]_n\cdot\text{Cl}$, NHR_2 and $(\text{CH}_2)_2\text{O}$, or $\text{NR}_2\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{Et}$ and $\text{Na}\cdot\text{EtOH}$: β -butylallyl-, b.p. 212 — $213^\circ/744$ mm., β -di-n-, b.p. 226 — $228^\circ/738$ mm., and -sec-butyl-aminoethyl alcohol, b.p. 224 — $266^\circ/745$ mm.; γ -di-n-propyl-, b.p. 210 — $220^\circ/750$ mm., and -n-butyl-, b.p. 247 — $248^\circ/759$ mm., β -diethyl-, b.p. 166 — $169^\circ/749$ mm., -butyl-, b.p. 112 — $114^\circ/20$ mm., and -allyl-aminopropyl alcohol, b.p. 145 — $147^\circ/123$ mm.; β -diethylamino-isobutyl, b.p. 132 — $135^\circ/45$ mm., and -heptyl alcohol, b.p. 107 — $109^\circ/10$ mm. The appropriate NH_2 -alcohol and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ or sec. base and ω -bromoalkyl p-nitrobenzoate give the following p-nitrobenzoate hydrochlorides: β -dimethyl-, m.p. 58° , di-n-, m.p. 133.5 — 134.5° , and -iso-propyl-, m.p. 162.5° , -n-, m.p. 92.5 — 93.5° , -iso-, m.p. 160 — 161° , and -sec-butyl- (base, m.p. 51 — 51.5°), and -isoamyl-, m.p. 123 — 124° , and β -butylallyl-aminopropyl, m.p. 117.5 — 118.5° ; γ -di-methyl-, m.p. 161° , -ethyl-, m.p. 189 — 190° , -n-, m.p. 147 — 148° , and -iso-propyl-, double m.p. 140° and 160° , -di-n-, m.p. 127.5 — 128.5° , and -iso-butyl-, m.p. 40.5 — 41.5° , and β -diethyl-aminopropyl, m.p. 155.6° ; δ -diethylaminobutyl, m.p. 159 — 160° ; ϵ -diethylaminoamyl, m.p. 142.3° . Reduction of the hydrochlorides by Fe in H_2O gives the following p-aminobenzoate hydrochlorides: β -dimethyl-, m.p. 183° ,

-*di-n*-, m.p. 201—202°, and -*iso-propyl*-, m.p. 166—167°, -*n*-, m.p. 169·5—170·5, -*iso*-, m.p. 198—199°, and -*sec-butyl*-, m.p. 188·5—190·5°, -*n*-, m.p. 154°, and -*iso-amyl*-, m.p. 152—152·5°, and β -*butylallyl-aminomethyl*-, m.p. 181—182°; γ -*di-methyl*-, m.p. 164·5°, -*ethyl*-, m.p. 161—162°, -*di-n*-, m.p. 181—182°, and -*iso-propyl*-, double m.p. 163·5° and 180—181°, -*n*-, double m.p. 124—126° and 149—150·5°, -*iso*-, m.p. 208—209°, and -*sec-butyl*-, m.p. 164·5—165·5°, -*n*-, m.p. 137°, and -*iso-amyl*-, m.p. 172—172·5°, and -*cyclohexyl*-, decomp. 270—280°, γ -*butylallyl*-, m.p. 143·5—144·5°, and β -*di-allyl*-, m.p. 182·3°, -*ethyl*-, m.p. 159—160°, and -*n-butyl-aminopropyl*-, m.p. 200°; δ -*diethylaminobutyl*-, m.p. 155—156°; ϵ -*diethylamino-amyl*-, m.p. 133—134°; β -*diethylamino-isobutyl*-, m.p. 171—172°, and -*heptyl*-, m.p. 118—119°. R. S. C.

Preparation of monoaminoalkyl *p*-aminobenzoates. S. D. GOLDBERG and W. F. WHITMORE (J. Amer. Chem. Soc., 1937, 59, 2280—2282).—NHPPhR and (CH₂)₂O give NHPPhR·[CH₂]₂·OH and thence the *p*-NO-derivative, which with conc. NaOH affords NHR·[CH₂]₂·OH in 35% over-all yield. Alcohols, NHR·[CH₂]₃·OH, are obtained from [CH₂]₃O or OH·[CH₂]₃·Br and NH₂R. The NH₂-alcohols are esterified with *p*-NO₂·C₆H₄·COCl and then reduced (Fe—HCl) to alkylaminoalkyl *p*-aminobenzoates, which are anaesthetics of low toxicity. The following are new: β -*n-amylaminoethyl alcohol*, b.p. 214—216°; γ -*ethyl*-, b.p. 181°, γ -*n-propyl*-, b.p. 199—200°, γ -*n-butyl*-, b.p. 213—215°, and γ -*amyl-aminopropyl alcohol*, b.p. 233°; β -*n-propyl*- (*hydrochloride*, m.p. 160°), β -*n*-, m.p. 75° (*hydrochloride*, m.p. 146°), and -*iso-butyl*- (*hydrochloride*, m.p. 192—194°), β -*n*-, m.p. 66° (*hydrochloride*, m.p. 152—153°), and -*iso-amyl-aminoethyl p-aminobenzoate* (*hydrochloride*, m.p. 148—150°); γ -*n-propyl*-, m.p. 70° (*hydrochloride*, m.p. 201—202°), -*butyl*-, m.p. 56° (*hydrochloride*, m.p. 196—197°), and -*amyl-aminopropyl p-aminobenzoate*, m.p. 76° (*hydrochloride*, m.p. 149—150°). R. S. C.

Effect of polar groups on esterification velocities of substituted benzoic acids.—See A., I, 36.

Variations in the sweetening power of saccharin. IV. Relative influences of the association of saccharin with substances containing the carbamide group.—See A., III, 68.

Effect of the simultaneous action of radiations of different frequencies on the bromination of cinnamic acid and stilbene.—See A., I, 40.

Preparation of 1-naphthonitrile. M. S. NEWMAN (J. Amer. Chem. Soc., 1937, 59, 2472).—92—93% yields are obtained from 1-C₁₀H₇Cl or -C₁₀H₇Br by CuCN in C₅H₅N at 220—250°. R. S. C.

5-Iodo-2-naphthoic acid. H. GOLDSTEIN and R. MATTHEY (Helv. Chim. Acta, 1937, 20, 1418—1421).—5:2-NH₂·C₁₀H₆·CN (I) is more profitably obtained by distilling a mixture of 5:2-NH₂·C₁₀H₆·SO₃Na with KCN at 270—325°/250—300 mm. than by reduction of 5:2-NO₂·C₁₀H₆·CN. (I) is transformed through the N₂-compound into 5-iodo-2-naphthonitrile, m.p. 148·5° (corr.), hydrolysed by H₂SO₄—AcOH—H₂O to 5-iodo-2-naphthoic acid, m.p. 264° (corr.), also obtained by first hydrolysing and then diazotising the nitrile. Its *Me* ester, m.p. 78°

(corr.), *Et* ester, m.p. 58·5° (corr.), *chloride*, m.p. 69—70° (corr.), *amide*, m.p. 196° (corr.), and *anilide*, m.p. 203° (corr.), are described. H. W.

Relative rates of decomposition of the potassium salts of *m*- and *p*-substituted dibenzhydroxamic acids. Lossen rearrangement. W. B. RENFREW, jun., and C. R. HAUSER (J. Amer. Chem. Soc., 1937, 59, 2308—2315).—The relative rates of decomp. of the K salts of RCO·NH·O·CO·R' in 0·1N-aq. NH₃ are inversely \propto the ionisation const. of RCO₂H and directly \propto that of R'CO₂H, in accordance with the view that the rate of the Hofmann and Lossen rearrangements depends on the release of X as a negative ion from [RC(O)·NX]⁻. The NH₃ destroys the PhNCO formed without affecting the rate of decomp. *Dibenzhydroxamic acids* are prepared in which R = *p*-OMe·C₆H₄ and R' = Ph, m.p. 162—164°, or *m*-NO₂·C₆H₄, m.p. 124—126°; R = *m*-OMe·C₆H₄ and R' = Ph, m.p. 118—120°; R = *p*-C₆H₄Me and R' = Ph, m.p. 161—162°, or *m*-NO₂·C₆H₄, m.p. 161—162°; R = *m*-C₆H₄Me and R' = Ph, m.p. 123—125°, or *m*-C₆H₄F, m.p. 114—116°; R = Ph and R' = *m*-NO₂·C₆H₄, m.p. 148—150°, Ph, m.p. 161—162°, *p*-OMe·C₆H₄, m.p. 135—137°, or *m*-C₆H₄F, m.p. 140—143°. R. S. C.

***p*- α -Hydroxyethylbenzoic acid.** G. KOMPPA (Ann. Acad. Sci. fenn., 1935, A, 44, No. 9, 3—6; Chem. Zentr., 1936, i, 3825).—*p*-Propenylbenzene, on ozonolysis in AcOH, yields an *ozonide*, m.p. about 180°, which decomposes to *p*-C₆H₄Ac·CO₂H, m.p. 200° (*phenylhydrazone*, m.p. 234°; *semicarbazone*, m.p. 209°); this is reduced (Na—Hg) to *p*- α -hydroxyethylbenzoic acid, m.p. 108—109° (*benzoate*, m.p. 124°; *acetate*, m.p. 93—94°). H. N. R.

Friedel—Crafts reaction. II. Condensation of the anhydrides of *as*-disubstituted succinic acids with benzene and toluene. III. Condensation of succinic anhydride with the methyl ethers of phenol and the cresols. R. D. DESAI and M. A. WALI (Proc. Indian Acad. Sci., 1937, 6, A, 135—143, 144—147; cf. A., 1937, II, 340).—II. Phenylsuccinic anhydride, AlCl₃, and PhMe at room temp. give more γ -*keto*- β -, m.p. 154°, than α -*phenyl*- γ -*p-tolylbutyric acid* (I), m.p. 150°, but in PhNO₂ (I) is the main product. Neither acid condenses with piperonal. KCN, *p*-C₆H₄Me·CO·CH·CHPh, and a little AcOH in EtOH give (I), which is further characterised by condensation with *o*-OH·C₆H₄·CHO in MeOH—HCl to a *pyrylium* derivative, m.p. >290°. *as*-Disubstituted succinic anhydrides, however, give only the α -substituted acids, a difference for which an electronic mechanism is postulated. *cyclo-Hexane-1-carboxylic-I-acetic anhydride* and AlCl₃ with C₆H₆, best without PhNO₂, give *Ph 1-carboxycyclohexylmethyl ketone*, m.p. 117° (*pyrylium* derivative, m.p. >290°), reduced (Clemmensen) to 1- β -phenylethylcyclohexane-1-carboxylic acid, m.p. 90°; with PhMe it gives *p-tolyl 1-carboxycyclohexylmethyl ketone*, m.p. 130° (*pyrylium* derivative, m.p. >290°), but in PhNO₂ some *p-tolyl 1-p-toluoylecyclohexylmethyl ketone*, m.p. 138° (*pyrylium* derivative, m.p. >290°), is also formed. 3-Methylcyclopentane-1-carboxylic-I-acetic anhydride gives similarly *Ph*, m.p. 147° (obtained less well in PhNO₂; *pyrylium* derivative,

m.p. $>290^\circ$, and *p*-tolyl 1-carboxy-3-methylcyclopentylmethyl ketone, m.p. 144° (obtained also in good yield in PhNO_2) (piperonylidene, a gum, and pyrylium derivative, m.p. $>290^\circ$), reduced to 1- β -phenyl-, m.p. 70° , and *p*-tolyl-ethyl-3-methylcyclopentane-1-carboxylic acid, m.p. 62° , respectively. *as*-Dimethylsuccinic anhydride with C_6H_6 gives γ -keto- γ -phenyl-, m.p. 172 – 173° (piperonylidene, a gum, and pyrylium derivative, m.p. $>290^\circ$), reduced to γ -phenyl- α -dimethylbutyric acid, m.p. 96° .

III. $(\text{CH}_2\text{CO})_2\text{O}$, AlCl_3 , and PhOMe in PhNO_2 give γ -keto- γ -*p*-anisylbutyric acid, new m.p. 148° (oxidised to *p*-anisic acid by NaOBr and reduced to γ -*p*-anisylbutyric acid, m.p. 62°), and $\alpha\delta$ -di-*p*-hydroxyphenyl-*n*-butane- $\alpha\delta$ -dione, m.p. 54° , oxidised to *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$ give similarly γ -keto-4-methoxy-3-methyl-, m.p. 150° , γ -keto-4-methoxy-2-methyl-, and -2-methoxy-5-methylphenylbutyric acid, respectively, characterised by oxidation and reduced to γ -4-methoxy-3-methyl-, m.p. 98 – 99° , γ -4-methoxy-2-methyl-, m.p. 92° , and γ -2-methoxy-5-methyl-phenylbutyric acid, m.p. 66° , respectively.

R. S. C.

Derivatives of substituted succinic acids. III. Action of alkaline sodium hypobromite on phenylsuccinamide and $\alpha\alpha'$ -dimethylsuccinamide. J. A. McRAE, A. W. WESTON, and C. F. HUBBS (Canad. J. Res., 1937, 15, B, 434–437; cf. A., 1937, II, 245).— $\text{COCl}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COCl}$, $\text{CO}_2\text{Me}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, or preferably phenylsuccinimide with NH_3 yields phenylsuccindiamide, m.p. 211° , which with NaOBr , followed by hydrolysis (NaOH), yields $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ whilst $(\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}_2)_2$ similarly gives 5:6-dimethyldihydro-uracil, m.p. 204 – 205° , also prepared from tiglic acid and $\text{CO}(\text{NH}_2)_2$.

F. R. G.

Bromo- and nitro-derivatives of naphthalic acid. H. G. RULE and S. B. THOMSON (J.C.S., 1937, 1764–1767).—Bromination of naphthalic anhydride (I) in oleum- H_2SO_4 or HNO_3 affords, not the 4-Br-derivative, as stated by Francesconi and Bargellini (A., 1903, i, 34), but 3-bromonaphthalic anhydride (II), m.p. 244° (3-bromonaphthalimide, m.p. 316° ; Me 3-bromonaphthalate, m.p. 105°), the constitution of which was confirmed by synthesis from 3-nitronaphthalic anhydride. Bromination in alkaline medium affords 4-bromonaphthalic anhydride (III), which undergoes homonuclear substitution on nitration to 4-bromo-3-nitronaphthalic anhydride, m.p. 231 – 232° , synthesised from 2-nitro-3-aminoacenaphthene by way of 3-bromo-2-nitroacenaphthene, m.p. 143° . Nitration of 4-nitronaphthalic anhydride affords mainly the 4:5- $(\text{NO}_2)_2$ -derivative. Bromination of (I) in presence of Fe affords a tribromonaphthalic anhydride (IV), m.p. 232° , also obtained from acenaphthenequinone or its 3-Br-derivative. Mercuration of (II) affords a mixture of bromonaphthoic acids from which was separated 3-bromo-1-naphthoic acid, m.p. 231 – 232° (Me ester, m.p. 59°), synthesised from 3:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$. (III) similarly affords 5:1- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{CO}_2\text{H}$, but (IV) yields a mixture of tribromonaphthoic acids which could not be separated.

Derivatives of (I) are characterised by condensation with *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$. Thus (I) and its 4:5- and 3:6-

$(\text{NO}_2)_2$ -derivatives afford respectively 1':8'-naphthoylene-, m.p. 206° , and 4':5'-, m.p. 370° , and 3':6'-, m.p. 301° , -dinitro-1':8'-naphthoylene-1:2-benziminazole.
E. G. B.

Condensation of opianic acid with dimethylaniline. B. M. BOGOSLOVSKI (J. Gen. Chem. Russ., 1937, 7, 1525–1526).— NPhMe_2 , opianic acid, and ZnCl_2 (4 hr. at 100°) yield 4':4''-bis(dimethylamino)-3:4-dimethoxyphthalophenone hydrochloride, m.p. 102.5 – 103° .
R. T.

Molecular resonance systems. VI. Colour phenomena in phthaleins. G. SCHWARZENBACH and O. HAGGER (Helv. Chim. Acta, 1937, 20, 1591–1600; cf. A., 1937, I, 415; II, 385).—Indicator consts. have been determined for phenolphthalein and several related compounds. The results are discussed in relation to the stability of the lactone ring and the p_H range in which colour change occurs. F. L. U.

Derivatives of dehydrocholic acid. L. BELTRAMI and A. MOSSINI (Boll. Chim.-farm., 1937, 76, 553–554).—Ethylenediamine mono- (unstable) and di-dehydrocholate, m.p. 214 – 216° (decomp.), and the theophylline derivative of the latter were prepared.
F. O. H.

Preparation of tetramethoxydiphenic acids. B. M. BOGOSLOVSKI and V. S. KRASNOVA (J. Gen. Chem. Russ., 1937, 7, 1543–1545).—2-Amino-3:4- or -5:6-dimethoxybenzoic acid in AcOH is diazotised at 0° , and the product is added to CuOH ; 3:3':4:4'-, m.p. 175 – 176° (anhydride, m.p. 172 – 173°), or 5:5':6:6'-tetramethoxydiphenic acid, m.p. 210.5 – 211.5° (anhydride, m.p. 195.5 – 196°), are obtained.
R. T.

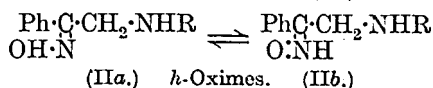
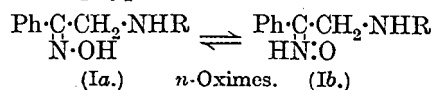
Derivatives of trans-decahydronaphthalene. K. A. N. RAO and T. S. KUPPUSWAMY (J. Annamalai Univ., 1937, 7, 22–26).—*trans*- β -Ketodecahydronaphthalene (I) with Na and isoamyl nitrite in abs. Et_2O yields oximino-*trans*- β -ketodecahydronaphthalene, decomp. 203° . Oxidation of (I) with SeO_2 in xylene yields 2:3- (or 1:2)-diketo-*trans*-decahydronaphthalene, b.p. 106 – $108^\circ/6$ mm. (disemicarbazone, m.p. 258°), whilst with Car's acid the peroxide of (I), m.p. 174° , is formed. Methylation ($\text{MeI}\cdot\text{NaNH}_2$) of (I) in abs. Et_2O yields 1-(or 3)-methyl-*trans*- β -ketodecahydronaphthalene, b.p. $117^\circ/16$ mm. (oxime, m.p. 132° ; semicarbazone, m.p. 201°), and bromination (Br in CCl_4) of (I) gives 1-(or 3)-bromo-, m.p. 148° , whilst with Br in AcOH dibromo-*trans*- β -ketodecahydronaphthalene (semicarbazone, decomp. 225°) is formed. *trans*- β -Hydroxydecahydronaphthalene (II) and (I) when treated with PCl_5 yield respectively β -chloro-, b.p. 126 – $128^\circ/38$ mm., and $\beta\beta$ -dichloro-*trans*-decahydronaphthalene, b.p. $112^\circ/18$ mm. Bromination (Br in CHCl_3) of (II) yields 1- (or 3-), b.p. $125^\circ/25$ mm., and 3-(or 1)-bromo-*trans*- β -hydroxydecahydronaphthalene, b.p. $185^\circ/25$ mm., whilst with PBr_3 , (II) affords β -bromo-*trans*-decahydronaphthalene, b.p. 143 – $145^\circ/40$ mm., which with Na or Cu in boiling xylene gives di- β -*trans*-decahydronaphthyl, b.p. $212^\circ/20$ mm.

J. D. R.

Transformation of unsaturated aliphatic acids into cyclopentenones. P. A. PLATTNER and A. S. PFAU (Helv. Chim. Acta, 1937, 20, 1474–1483).—

The transformation of unsaturated acids into lactones is accompanied by the formation of ketones. The formation of the latter compounds is facilitated by the action of conc. acids, e.g., H_2SO_4 , at $<100^\circ$ following the technique of lactonisation, by heating with catalytic quantities of strong acids or strongly acidic salts ($p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$, $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$, H_3PO_4 , ZnCl_2 , etc.) with removal of the products by distillation as they form, and by passage of the gaseous or liquid acid alone or mixed with a gas or an indifferent solvent over a suitably heated catalyst (H_3PO_4 , H phosphates, silicates, SiO_2 gel, amphoteric oxides such as Al_2O_3 or their mixtures). Thus undecenoic acid is converted by SiO_2 gel at 350° into 2-hexyl- Δ^2 -cyclopentenone (semicarbazone, m.p. 196°), transformed in CCl_4 into an ozonide, which with $0.5\text{N}\cdot\text{KOH}$ and H_2O_2 affords heptoic and succinic acid. It is hydrogenated (Ni in EtOH at 20°) to 2-hexylcyclopentanone (I), b.p. $117\text{--}119^\circ/10\text{ mm.}$ (CHPh derivative, m.p. $59\text{--}60^\circ$). The CHPh derivatives of 2-isoamyl-, 2-heptyl-, and 2-cyclopentyl-cyclopentanone have m.p. $84\text{--}85^\circ$, $66\text{--}67^\circ$, and $97\text{--}98^\circ$, respectively). The ketonic fraction contains also 2-hexyl- Δ^3 -cyclopentenone, b.p. $117^\circ/10\text{ mm.}$ (semicarbazone, m.p. $181\text{--}182^\circ$), hydrogenated to (I). The neutral products of the attempted lactonisation of decenoic acid contain 2-n-amyl- Δ^2 -cyclopentenone, b.p. $108^\circ/10\text{ mm.}$ (semicarbazone, m.p. $199\text{--}200^\circ$), ozonised to hexoic and succinic acids. γ -Methyldecenoic acid analogously yields 3-methyl-2-amyl- Δ^2 -cyclopentenone, the odour of which is very similar to that of jasmone. Undecic acid is unchanged when distilled with $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ under atm. pressure. H. W.

Isomerism of phenacylaminoximes. M. BUSCH and F. STRÄTZ [with P. UNGER, R. REICHOLO, and B. ECKARDT] (J. pr. Chem., 1937, [ii], 150, 1—39).—The chemical and physical properties of the phenacyl- p -toluidineoximes (I), show that tautomeric equilibria of the following types occur in their solutions:



(Ia) accounts for the Beckmann transformation. n -Oximes can condense with aldehydes only in the Ia form with production of oxidiazines. Oxidation and complex salt formation appear impossible with either form. With h -oximes the condensation with aldehydes, oxidation, and formation of complex salts occur according to IIb. Only the alkyl derivatives are derived from IIa. The difference in the dissociation consts. of isomeric oximes is plausibly explained by the hypothesis that the equilibrium of n -oximes is displaced towards Ia and that of h -oximes towards IIb. The differing acidity points in the same direction. With some isomerides relatively great differences in p_{H} are observed, the n -forms being the more strongly acidic. (I) are not suitable substances for study of the change since the m.p. [n -oxime (II), m.p. $96\text{--}5^\circ$; n -oxime (III), m.p. 97°] lie too close together (cf. A., 1930, 603). With excess of CH_2O (III) readily gives

phenyl- p -tolylloxidiazine (IV),

$\text{N}\begin{array}{c} \text{CPh}\cdot\text{CH}_2 \\ \text{O}\text{---}\text{CH}_2 \end{array}\text{N}\cdot\text{C}_6\text{H}_4\text{Me-}p$, m.p. 105° , whilst impure (II) affords a mixture of (III) and 4-phenyl-1- p -tolylglyoxaline 3-oxide (V),

$\text{CPh}\text{---}\text{CH}_2\text{---}\text{N}\cdot\text{C}_6\text{H}_4\text{Me-}p$, m.p. $223\text{--}5^\circ$. (III) is indifferent towards FeCl_3 , whereby (II) is transformed into dehydrophenacyl- p -toluidineoxime,

$\text{N}(\text{C}_6\text{H}_4\text{Me})\text{---}\text{CH}_2\text{---}\text{CPh}\text{---}\text{NO}$, m.p. 225° (decomp.), which does not give a nitrosoamine or show basic or acidic properties. It is hydrolysed by boiling dil. H_2SO_4 and reduced by Zn dust and AcOH to the compound, $\text{N}(\text{C}_6\text{H}_4\text{Me})\text{---}\text{CH}_2\text{---}\text{CPh}\text{---}\text{N}$,

m.p. $191\text{--}192^\circ$ (decomp.) (hydrochloride, decomp. $>238^\circ$). The anti-oxime does not give a complex salt with FeCl_3 , whereas with CoCl_2 the substance, $(\text{C}_{15}\text{H}_{15}\text{ON})_2$, CoCl_2 , slow decomp. 240° after darkening at 225° , results. Benzoylation of both oximes (Schotten-Baumann) affords the Bz_2 derivative (VI), m.p. 134° , of phenacyl- p -toluidineoxime, also derived from (IV) or (V) with elimination of PhCHO . With a limited amount of BzCl in $\text{C}_5\text{H}_5\text{N}$ the product from either oxime is the compound,

$\text{OH}\cdot\text{N}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{NBz}\cdot\text{C}_6\text{H}_4\text{Me-}p$, m.p. $174\text{--}5^\circ$ (decomp.), obtained also by the partial hydrolysis of (VI) and shown by hydrolysis to be derived from (III). Similar relationships are observed with phenacyl-anilineoxime, of which the *syn*-form, m.p. $106\text{--}107^\circ$, and the non-homogeneous *anti*-form, m.p. $90\text{--}94^\circ$, are isolated. Oximation of phenacylmethylaniline gives a mixture of the two oximes which is separated with difficulty. Phenacyl- p -anisidine gives an h -oxime (VII), m.p. 125° , which gives a marked reaction with FeCl_3 and an n -oxime (VIII), m.p. 86° , which do not differ in absorption spectrum. Attempted interconversions were unsuccessful. (VIII) is converted by PCl_5 in Et_2O at -10° into p -methoxyanilinoacetanilide, m.p. 57° (hydrochloride, m.p. 216°), and hence has the *syn*-configuration; under similar conditions (VII) gives essentially dehydrophenacyl- p -anisidine-oxime, m.p. 223° . PhCHO and (VIII) give diphenyl- p -anisylloxidiazine (IX),

$\text{N}\begin{array}{c} \text{CPh}\cdot\text{CH}_2 \\ \text{O}\text{---}\text{CHPh} \end{array}\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe-}p$, m.p. $146\text{--}5^\circ$, in 96.5% yield, whereas (VII) yields diphenyl- p -anisylglyoxaline oxide, m.p. 199° , which is neither basic nor acidic, loses PhCHO when boiled with dil. H_2SO_4 , and loses 1 H_2O when heated with $\text{KOH}\text{---}\text{EtOH}$ at 60° giving the substance, $\text{C}_{22}\text{H}_{18}\text{ON}_2$, m.p. $109\text{--}110^\circ$. (IX) is isomerised to (X) by boiling glacial AcOH . With excess of CH_2O in EtOH (VIII) and (VII) afford phenyl- p -anisylloxidiazine, m.p. 127° , and 4-phenyl-1- p -anisylglyoxaline 3-oxide, m.p. 187° , respectively. (VII) gives a Co complex, decomp. about 225° . $\text{KOH}\text{---}\text{EtOH}$, CH_2PhCl , and (VIII) give the dibenzyl derivative, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ (XI), m.p. 58° , whereas (VII) gives the isomeric compound (XII), m.p. 99° . Benzyl- p -anisidine is transformed by CH_2BzBr in EtOH at $>15^\circ$ into phenacylbenzyl- p -anisidine (XIII), m.p. $101\text{--}102^\circ$, converted by $\text{NH}_2\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ into a mixture of (XI) and (XII). (VIII) and CH_2PhCl in EtOH in absence of alkali yield the N -benzyl derivative,

$\text{OH}\cdot\text{N}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{N}(\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CH}_2\text{Ph}$, m.p. $>105^\circ$, whilst (VII) gives the isomeric compound, m.p. 118° . The oximation of (XII) is described. *Phenacyl-o-anisidineoxime* has m.p. $129\text{--}130^\circ$. *Phenacyl-o-toluidine*, m.p. 91° , gives an *n-oxime*, m.p. 92° , which by reason of *o*-Me does not react with PhCHO , and a non-homogeneous *h-oxime*, m.p. 63° , which is readily oxidised and reacts with FeCl_3 , CH_2BzBr and $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ slowly yield *phenacyl-o-chloroaniline*, m.p. 105° , which yields a single *oxime*, m.p. 115° , which could not be condensed with PhCHO . *Phenacyl-m-chloroaniline*, m.p. 143° , gives an *n-oxime*, m.p. 112° , and an *h-oxime*, m.p. 114° . The *n*- and *h-phenacyl-p-chloroanilineoximes* have m.p. 115° and 125° , respectively. *m-Nitrophenacyl-o-toluidine* gives an *n-oxime*, m.p. 150° , and *h-oxime*, m.p. 178° , the former of which condenses with PhCHO to (?) *phenyl-o-tolyl-m'-nitrophenyloxidiazine*, m.p. 167° , whereas the latter does not react. Both oximes are converted by cold Ac_2O into the same Ac_1 derivative, m.p. 180° , and by the hot reagent into the same Ac_2 compound, m.p. 103° . *m-Nitrophenyl-p-anisidine*, m.p. 139° , affords a yellow *n-oxime*, m.p. 126° (whence *phenyl-m-nitrophenyl-p-anisilyloxidiazine*, m.p. 132°), and a red *h-oxime*, m.p. 138° , which gives a dark violet colour with FeCl_3 and is transformed by PhCHO into the *glyoxaline oxide*, $\text{C}_{22}\text{H}_{19}\text{O}_4\text{N}_3$, m.p. 206° . *m-Nitrophenacyl-p-toluidine*, m.p. 153° , appears to give a colourless *oxime*, m.p. 88° , an *n-oxime*, stable orange crystals, m.p. 123° , or unstable pale yellow crystals, m.p. (indef.) $113\text{--}115^\circ$, and an *h-oxime*, m.p. 139° . With the requisite aldehyde the former yields *m-nitrophenyl-p-tolyl*, m.p. $149\cdot5^\circ$, *m-nitrophenyl-p-tolylolethyl*, m.p. about 92° after becoming yellow at 90° , and *phenyl-m-nitrophenyl-p-tolyl*, m.p. 134° , -*oxidiazine* whereas the latter affords *m-nitrophenyl-p-tolyl*, m.p. 225° , *m-nitrophenyl-p-tolylolethyl*, m.p. 189° , and *phenyl-m-nitrophenyl-p-tolyl*, m.p. 224° , -*glyoxaline oxide*. According to conditions both oximes are converted by Ac_2O into the same Ac_1 , m.p. 218° , or Ac_2 , m.p. 105° , derivative. *Anilinobenzoin-h-oxime*, m.p. 163° , and *n-oxime*, m.p. 133° , do not react with FeCl_3 . The latter reacts very readily and the former only in boiling EtOH containing HCl with PhCHO giving *tetraphenyloxidiazine*, m.p. 250° ; isomerisation of the *h*- to the *n-oxime* does not occur in boiling EtOH containing HCl in absence of PhCHO . $\text{o-C}_6\text{H}_4\text{Ac}\cdot\text{NH}_2$ gives only one *oxime* (XIV), m.p. $108\text{--}109^\circ$, which gives an intense dark red colour with FeCl_3 . It reacts readily with PhCHO containing a little BzOH giving *2-phenyl-4-methyl-1:2-dihydroquinazoline 3-oxide* (hydrochloride), which has 1 active H and gives a *NO*-derivative, m.p. 109° (decomp.). The ring is unstable since the action of BzCl in NaOH or $\text{C}_5\text{H}_5\text{N}$ leads to *o-benzamidoacetophenoneoxime benzoate*, m.p. 135° , hydrolysed by cold alkali to *o-benzamidoacetophenoneoxime*, m.p. 181° . $\text{m-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and (XIV) give *2-m-nitrophenyl-4-methyl-1:2-dihydroquinazoline 3-oxide*, m.p. 175° . With COCl_2 in PhMe (XIII) yields *2-keto-4-methylquinazoline 3-oxide*, m.p. 227° (decomp.). In general the *h-oximes* have the *anti*-Me configuration or the amine-oxide constitution and give the reaction with FeCl_3 , which therefore distinguishes the steric form of the phenacylamineoximes. Exceptions are the oximes

of *o*-substituted arylamine derivatives of phenacylamine and those in which the imide-H of the alkylamino-ketone is replaced by alkyl or acyl. Frequently only one oxime is here observed and the FeCl_3 action does not occur.

H. W.

Stereochemistry of $\alpha\beta$ -unsaturated ketones.

E. BARONI (Österr. Chem.-Ztg., 1937, 40, 497).—The oximes of styryl Et ketone and γ -keto- β -benzylidenebutane have been obtained each in two forms. The labile, *anti*-varieties readily lose H_2O and give 2-substituted quinolines. The stable *syn*-forms give isoquinoline derivatives.

H. W.

periNaphthindone. I. Preparation of perinaphthindone and its oxonium compounds.

G. B. ZILBERMAN and S. M. BARKOV (J. Gen. Chem. Russ., 1937, 7, 1733–1737).—The oxonium salts $\text{R}_2\cdot\text{HFeCl}_4$, m.p. $160\text{--}166^\circ$ (decomp.), $\text{R}_2\cdot\text{SnCl}_4$, $\text{R}_2\cdot\text{SbCl}_5$, $\text{R}_2\cdot\text{H}_4\text{Fe}(\text{CN})_6$, and $\text{R}_2\cdot\text{HClO}_4$ [R = perinaphthindone (I)] are described. (I) yields peritrimethylenenaphthalene when reduced with Zn in AcOH , followed by distillation from Zn dust.

R. T.

Action of alkalis on aromatic ketones.

P. N. FEDOSEEV (J. Gen. Chem. Russ., 1937, 7, 1364–1365).—The following ketones have been prepared from BzCl or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COCl}$ and the appropriate substituted hydrocarbon in CS_2 in presence of AlCl_3 : 2:4'-dimethyl-5-isopropyl-, b.p. $342\text{--}343^\circ$; 2:5-diethyl-, b.p. $332\text{--}334^\circ$; 4'-methyl-2:5-diethyl-, b.p. $330\text{--}331^\circ$; 4'-methyl-2:4:6-triphenyl-, m.p. 195° ; 2(5)-methyl-5(2)-ethyl-, b.p. 330° ; 2(5):4'-dimethyl-5(2)-ethyl-benzophenone, b.p. 340° . On fusion with KOH the ketones dissociate to yield BzOH or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ and substituted benzene hydrocarbons.

R. T.

Phenanthrene derivatives. VII. Cyclisation of β -phenanthrylpropionic acids.

W. E. BACHMANN and M. C. KLOETZEL (J. Amer. Chem. Soc., 1937, 59, 2207–2213).—Partly a more detailed account of work previously reviewed (A., 1935, 1117). The appropriate aldehydophenanthrene (A) and $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ give β -1-, -2-, -3-, and -10-phenanthrylacrylic acids, m.p. 262° (lit. 259°), $245\text{--}246^\circ$, $273\text{--}274^\circ$, and $231\text{--}233\cdot5^\circ$, respectively (*Me* esters, m.p. $130\text{--}131^\circ$, $104\cdot5\text{--}105\cdot5^\circ$, $106\text{--}107^\circ$, and $108\text{--}109^\circ$, respectively), which are reduced (2% Na-Hg , aq. KOH) to β -1- (I), -2- (II), -3- (III), and -10- (IV)-phenanthrylpropionic acids, m.p. $188\cdot5\text{--}189^\circ$, $177\text{--}177\cdot5^\circ$, $158\cdot5\text{--}159\cdot5^\circ$, and $173\text{--}174^\circ$, respectively (*Me* esters, m.p. $90\text{--}91^\circ$, $82\text{--}83^\circ$, $63\text{--}64^\circ$, and $72\text{--}73^\circ$, respectively). The latter acids are also synthesised (malonic ester method) from the phenanthrylmethyl bromides, which are prepared from the carbinols [generally obtained by reduction of (A) with $\text{CHPh}_2\cdot\text{OMgBr}$ in $\text{Et}_2\text{O-C}_6\text{H}_6$] and PBr in CCl_4 . 1-Phenanthrylcarbinol, m.p. $166\text{--}167^\circ$, and its bromide, m.p. 97° , are new; 3- and 10-phenanthrylmethyl bromides have m.p. $117\cdot5^\circ$ (lit. $114\cdot5\text{--}115^\circ$) and $118\cdot5\text{--}119\cdot5^\circ$ (lit. $103\text{--}103\cdot5^\circ$), respectively, whilst β -1-, -2-, -3-, and -10-phenanthrylethane- $\alpha\alpha$ -dicarboxylic acids have m.p. (decomp.) 190° , 180° , 187° , and $185\text{--}188^\circ$, respectively. (I) (as chloride) with AlCl_3 in PhNO_2 at 0° gives 4% of 3'-keto-1:2-cyclopentenophenanthrene, m.p. $195\text{--}196^\circ$, and 25% of 6-keto-

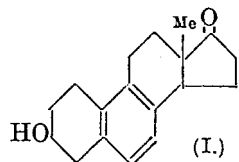
4:5-dihydrobenzanthrene, m.p. 130.5—131.5°, which are reduced (Clemmensen) to 1:2-cyclopentenophenanthrene (V) and 4:5-dihydrobenzanthrene (VI), m.p. 76—77° (picrate, m.p. 123—124°), respectively. (II) (as chloride) and SnCl_4 in PhNO_2 at 80° afford 1'-keto-1:2-cyclopentenophenanthrene, m.p. 183—184°, reduced to (V). (III) (as chloride) with SnCl_4 in CS_2 or AlCl_3 in PhNO_2 gives (cf. *loc. cit.*) 3'-keto-3:4-cyclopentenophenanthrene, m.p. 142°, oxidised (70% HNO_3) to 1:2:3:4- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$ and reduced (Clemmensen) to 3:4-cyclopentenophenanthrene, m.p. 73.5—75° (picrate, m.p. 135.5—136°), which also exists in a form of m.p. 60°. (IV) (as chloride) and AlCl_3 in PhNO_2 afford a mixture (not separated) of 4-keto-5:6-dihydrobenzanthrene and 1'-keto-9:10-cyclopentenophenanthrene, since reduction gives (VI) and 9:10-cyclopentenophenanthrene (VII), m.p. 149—150° (picrate, m.p. 161.5—162°). 1-o-Diphenylcyclopentanol, m.p. 90.5—91.5° (from $\text{o-C}_6\text{H}_4\text{Ph-MgBr}$ and cyclopentanone), is dehydrated (KHSO_4 at 160°) to 1-o-diphenyl- Δ^1 -cyclopentene, which with AlCl_3 in CS_2 at 0° affords, not (VII), but 9-fluorospirocyclopentane, m.p. 91° (resistant to dehydrogenation by S, Se, and Pt). The prep. of 3-aldehydophenanthrene is improved.

H. B.

Action of aluminium chloride on phenyl- α -naphthylacetyl chloride. C. F. KOELSCH and H. J. RICHTER (J. Amer. Chem. Soc., 1937, 59, 2165—2166).—The product obtained from $\alpha\text{-C}_{10}\text{H}_7\text{-CHPh-COCl}$ and AlCl_3 (method improved) (cf. A., 1936, 65) is 7-phenylacenaphthene, since with CrO_3 or $\text{O}_2\text{-KOH}$ it gives 8:1- $\text{C}_{10}\text{H}_6\text{Bz-CO}_2\text{H}$. It cannot be methylated, reacts as a ketone with MgPhBr to give an oil dehydrated to 7:8-diphenylacenaphthylene, but gives the red benzoate, m.p. 143—145°, of the enolic form.

R. S. C.

Artificial production of oestrogenic substances from certain sterols. III. Structure and properties of a synthetic analogue of the follicular ovarian hormone. I. REMESOV (Rec. trav. chim., 1937, 56, 1093—1102).—The substance $\text{C}_{18}\text{H}_{22}\text{O}_2$ previously synthesised (A., 1936, 1505) and described by Marker *et al.* (*ibid.*, 1256) as oestrone is shown by spectrophotometric analysis to be 3-hydroxy-17-keto-5:7:9-oestratriene (I), m.p. 248—248.5°, $[\alpha]_D^{25} +162^\circ$ in CHCl_3 , an isomeride of oestrone. The acetate, m.p. 112—116°, benzoate, m.p. 202°, oxime, m.p. 236°, and semicarbazone, m.p. 260—262°, are described.



J. D. R.

Sex hormones. XXVII. 17-cis- and 17-trans-Isomeric diols and hydroxyketones and androstane and androstene. L. RUZICKA and H. KÄRIG (Helv. Chim. Acta, 1937, 20, 1557—1564).— Δ^5 -Androstene-3-trans-17-trans-diol 3-acetate 17-hexahydrobenzoate, m.p. 134—135°, transformed by partial hydrolysis into androstane-3-trans-17-trans-diol 17-hexahydrobenzoate, m.p. 167.5—168°; this is oxidised by CrO_3 in AcOH to androstane-17-trans-ol-3-one 17-hexahydrobenzoate, m.p. 164—165°, hydrolysed to

androstane-17-trans-ol-3-one (dihydrotestosterone), m.p. 181.5—182.5° (corr.). Similarly, Δ^5 -androstene-3-trans-17-cis-diol 3-acetate 17-benzoate is hydrogenated to androstane-3-trans-17-cis-diol 3-acetate 17-hexahydrobenzoate, an oil, whence androstane-3-trans-17-cis-diol 17-hexahydrobenzoate, m.p. 208.5—209.5° (also obtained by hydrogenation of Δ^5 -androstene-3-trans-17-cis-diol 17-benzoate), androstan-17-cis-ol-3-one 17-hexahydrobenzoate, m.p. 137.5—138°, and androstan-17-cis-ol-3-one (I), m.p. 179.5—180° (acetate, m.p. 150—151°). Hydrogenation (PtO_2 in AcOH containing HBr at 65°) of (I) affords androstane-3-cis-17-cis-diol, m.p. 227—228°. Comparison of the physiological activity of the diols shows the importance of the *cis*-configuration of OH at C_{13} , and of the *trans*-position of OH at C_{17} .

H. W.

Manufacture of tertiary carbinols of the cyclopentanopolyhydrophenanthrene series.—See B., 1937, 1270.

Manufacture of reduction products derived from dehydroandrosterone.—See B., 1937, 1270.

Manufacture of pregnenediones.—See B., 1937, 1270.

Halogen derivatives of acenaphthene. II. M. M. DASCHESKI and A. P. KARISCHIN (Prom. Org. Chim., 1937, 4, 406—410).—The products of oxidation of halogen-substituted acenaphthenes by chromates in AcOH are bisacenaphthenediones, acenaphthenequinones, or naphthalic acids, in yields depending on the conditions of oxidation, and on the nature or no. of halogen atoms in the mol. Thus 3:4-dichloro-acenaphthene gives 3:4:3':4'-tetrachlorodiacenaphthylidenedione, not melting at 400°, 3:4-dichloro-acenaphthenequinone, m.p. 305°, and 4:5-dichloro-naphthalic acid, also obtained by oxidation of 3:4:7:7':8-pentachloroacenaphthene, m.p. 198—199° (by chlorination of acenaphthene). A boiling solution of acenaphthene in boiling EtOH is brominated with Br vapour, to yield 3-bromo- and 3:4-dibromo-acenaphthene, m.p. 140°, b.p. 203°/3 mm., from which 3:3'-dibromo- and 3:4:3':4'-tetrabromodiacenaphthylidenediol, m.p. >400°, 3-bromo- and 3:4-dibromo-acenaphthenequinone, m.p. 258.8°, and 4-bromo- and 4:5-dibromo-naphthalic acid, m.p. 260°, are obtained by oxidation as above.

R. T.

Chalkones. Reactivity of some aryl alkoxy-styryl ketones and their dihalides. S. M. NADKARNI, A. M. WARRIAR, and T. S. WHEELER (J.C.S., 1937, 1798—1804).—Aryl β -alkoxyphenylethyl ketones ($\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{R}'$; $\text{R} = p\text{-tolyl}$, $\text{R}' = p\text{-anisyl}$ or 3:4- $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3$) and their $\alpha\beta$ -dihalides are readily halogenated in the alkoxyphenyl nucleus to $\alpha\beta$ -dihalogenoketones ($\text{R}\cdot\text{CO}\cdot\text{CHX}\cdot\text{CHX}\cdot\text{R}''$; $\text{R}'' = \text{halogenated R}'$). The position of the halogen in R'' is shown by conversion by KI in COMe_2 into halogeno-chalkones, $\text{R}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{R}''$, which were synthesised from the corresponding acetophenones. With MeOH or EtOH the dihalides, $\text{R}\cdot\text{CO}\cdot\text{CHX}\cdot\text{CHX}\cdot\text{R}'''$ (I) ($\text{R}''' = \text{R}'$ or R'') afford $p\text{-tolyl } \alpha\text{-halogeno-}\beta\text{-alkoxy-}\beta\text{-phenylethyl ketones}$, $\text{R}\cdot\text{CO}\cdot\text{CHX}\cdot\text{CHR}'''\cdot\text{OR}''''$ (II) ($\text{R}'''' = \text{OMe}$ or OEt) by replacement of the labile α -halogen atom. The β -alkoxy-group in (II) is also labile and is replaced by Br by action of HBr . With

KCN-EtOH in the cold (I) give chalkones $R\cdot CO\cdot CH\cdot CHR''$ and in the warm propionitriles $R\cdot CO\cdot CH_2\cdot CHR''\cdot CN$. *p*-Tolyl $\alpha\beta$ -dichloro- β -3-chloro-*p*-anisylethyl ketone, m.p. 125°, however, reacts anomalously in the cold to give *p*-tolyl α -3-dichloro-4-methoxystyryl ketone, m.p. 115°, the KCN acting as alkali. On hydrolysis the nitriles afford propionic acids, $R\cdot CO\cdot CH_2\cdot CHR''\cdot CO_2H$. With bases (I) give α -halogenostyryl derivatives, $R\cdot CO\cdot CX\cdot CHR''$, also obtained by heating (II). With excess of base β -alkoxystyryl ketones, $R\cdot CO\cdot CH\cdot CR''\cdot OR''$, may be formed, depending on the groups present. These are also formed by action of Na alkoxides on (II) and are hydrolysed to tautomeric diketones, $R\cdot CO\cdot CH_2\cdot CO\cdot R''$. With NH_2OH (I) give isooxazoles $R''\cdot C\leq\frac{CH\cdot CR}{O-N}$, and with $CH_2Ac\cdot CO_2Et$, *Et* 6-alkoxyphenyl-4-*p*-tolyl- Δ^3 -cyclohexen-2-one-1-carboxylates, hydrolysed to the corresponding hexenones. *o*-Hydroxy- or *o*-acetoxy-aryl alkoxystyryl ketone dibromides yield benzylidenecoumaranones or flavones (III) on treatment with bases, depending probably on whether or no intermediate β -alkoxy-compounds are formed. This provides a synthesis of (III) from chalkone dibromides.

The following are described. *p*-Tolyl $\alpha\beta$ -dichloro-, m.p. 142°, $\alpha\beta$ -dibromo-, m.p. 172°, α -chloro- β -methoxy-, m.p. 107°, α -chloro- β -ethoxy-, m.p. 103°, α -bromo- β -methoxy-, m.p. 114°, α -bromo- β -ethoxy-, m.p. 105°, and α -chloro- β -bromo-, m.p. 154°, - β -*p*-anisylethyl ketones. *p*-Tolyl $\alpha\beta$ -dibromo- β -3-chloro-, m.p. 176°, and -3-bromo-, m.p. 176°, $\alpha\beta$ -dichloro- β -3-bromo-, m.p. 126°, α -chloro- β -methoxy- β -3-chloro-, m.p. 108°, - β -ethoxy- β -3-chloro-, m.p. 128°, - β -ethoxy- β -3-bromo-, m.p. 128°, - β -bromo- β -3-chloro-, m.p. 157°, and - β -bromo- β -3-bromo-, m.p. 161°, β -bromo- β -methoxy- β -3-chloro-, m.p. 126°, - β -methoxy- β -3-bromo-, m.p. 101°, and - β -ethoxy- β -3-bromo-, m.p. 103°, -*p*-anisylethyl ketones. *p*-Tolyl $\alpha\beta$ -dichloro-, m.p. 140°, $\alpha\beta$ -dibromo-, m.p. 144°, α -chloro- β -methoxy-, m.p. 94°, - β -ethoxy-, m.p. 95°, and β -bromo-, m.p. 137°, α -bromo- β -methoxy-, m.p. 120°, and - β -ethoxy-, m.p. 115°, - β -3:4-methylenedioxyphenylethyl ketones. *p*-Tolyl $\alpha\beta$ -dibromo- β -6-chloro-, m.p. 169°, and -6-bromo-, m.p. 175°, $\alpha\beta$ -dichloro- β -6-bromo-, m.p. 160°, and -6-chloro-, m.p. 157°, α -chloro- β -methoxy- β -6-chloro-, m.p. 114°, - β -ethoxy- β -6-chloro-, m.p. 95°, and - β -bromo- β -6-chloro-, m.p. 165°, α -bromo- β -methoxy- β -6-bromo-, m.p. 121°, and - β -ethoxy- β -6-bromo-, m.p. 104°, -3:4-methylenedioxyphenylethyl ketones. *p*-Tolyl 3-chloro-, m.p. 114°, 3-bromo-, m.p. 122°, α -chloro-, m.p. 98°, α -bromo-, m.p. 102°, 3-chloro- α -bromo-, m.p. 117°, α -chloro-3-bromo-, m.p. 107°, and α :3-dibromo-, m.p. 114°, -4-methoxystyryl ketones. *p*-Tolyl 6-chloro-, m.p. 139°, 6-bromo-, m.p. 150°, α -chloro-, m.p. 85°, α -bromo-, m.p. 80° (oxime, m.p. 164°), α :6-dichloro-, m.p. 114°, 6-chloro- α -bromo-, m.p. 130°, α -chloro-6-bromo-, m.p. 124°, α :6-dibromo-, m.p. 130°, and 6-bromo- β -methoxy-, m.p. 107°, and - β -ethoxy-, m.p. 127°, -3:4-methylenedioxy-styryl ketones. β -*p*-Toluoxy- α -3-bromo-*p*-anisyl-, m.p. 135°, - α :3:4-methylenedioxyphenyl-, m.p. 115°, - α :6-bromo-3:4-methylenedioxyphenyl-, m.p. 149°, and - α :3-chloro-*p*-anisyl-, m.p. 144°, -propionitriles. β -*p*-Toluoxy- α :3:4-methylenedioxyphenyl-, m.p. 160°, and - α :6-bromo- α :3:4-

methylenedioxyphenyl-, m.p. 188°, -propionic acids. 3-Chloro-*p*-anisyl-, m.p. 135° (*Cu* salt, m.p. 258°), 3-bromo-*p*-anisyl-, m.p. 122°, 3:4-methylenedioxybenzoyl-, m.p. 114° (*Cu* salt, m.p. 268°), and 6-bromo-3:4-methylenedioxybenzoyl-, m.p. 110°, -*p*-toluoxy-methanes. 5-(3':4'-Methylenedioxyphenyl)-, m.p. 135°, and 5-(6'-bromo-3':4'-methylenedioxyphenyl)-, m.p. 127°, -3-*p*-tolylisooxazoles. *Et* 6-*m*-chloro-, m.p. 136°, and 6-*m*-bromo-, m.p. 123°, -*p*-anisyl-, 6-(3':4'-methylenedioxyphenyl)-, m.p. 145°, 6-(6'-chloro-3':4'-methylenedioxyphenyl)-, m.p. 154°, and 6-(6'-bromo-3':4'-methylenedioxyphenyl)-, m.p. 167°, -4-*p*-tolyl- Δ^3 -cyclohexen-2-one-1-carboxylates. 5-*m*-Chloro-, m.p. 120°, and 5-*m*-bromo-, m.p. 122°, -*p*-anisyl-, 5-(3':4'-methylenedioxyphenyl)-, m.p. 130°, 5-(6'-chloro-3':4'-methylenedioxyphenyl)-, m.p. 151°, and 5-(6'-bromo-3':4'-methylenedioxyphenyl)-, m.p. 153°, -3-*p*-tolyl- Δ^2 -cyclohexenones. *o*-Hydroxyphenyl $\alpha\beta$ -dibromo-, m.p. 145°, and α -bromo- β -ethoxy-, m.p. 107°, - β -3:4-methylenedioxy-styryl ketones.

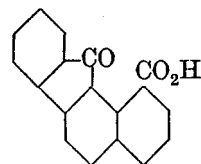
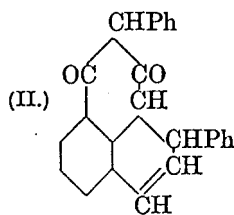
E. G. B.

Cationoid reactivity of aromatic compounds.

IV. Hydroxylation of *ms*-benzanthrone. W. BRADLEY and G. V. JADHAV (J.C.S., 1937, 1791—1792).—Hydroxylation of *ms*-benzanthrone with KOH and an oxidant affords a mixture of 2- and 4- (boroacetate, decomp. 268°) -hydroxy-*ms*-benzanthrone, thus providing a case of replacement by OH of H situated *para* and *ortho* to CO in the same reaction.

E. G. B.

periNaphthindene series. II. Action of lithium phenyl on 8-phenylperinaphthindane-7:9-dione. C. F. KOELSCH and R. H. ROSENWALD (J. Amer. Chem. Soc., 1937, 59, 2166—2169; cf. A., 1936, 1256).—8-Phenylperinaphthindane-7:9-dione (I) reacts with LiPh by 1:4-addition to the enolic form to give the enolic form, m.p. 178.5°, of 1:8-diphenyl-1:9a-dihydroperinaphthindane-7:9-dione (II), since dehydrogenation of the product by O_2 —



KOH, distillation at 15 mm., or, best, by *p*-benzoquinone gives 1:8-diphenylperinaphthindane-1:9-dione (III), m.p. 152—154° (*Na* salt), oxidised by alkaline $KMnO_4$ to 8-phenylglyoxalyl-7(or 2)-phenyl-1-naphthoic acid, m.p. 199—200° (gives no Me ether or quinoxaline derivative, but is cleaved by alkaline H_2O_2). With CrO_3 this acid gives BzOH and 2-phenyl-naphthoic acid, m.p. 239—240°, which is sulphonated by H_2SO_4 and unchanged by $POCl_3$, but with $AlCl_3$ in C_6H_6 gives chrysoketone-10-carboxylic acid (IV), m.p. 290—297° (decomp.) (*Me* ester, m.p. 164°), decarboxylated by distillation in vac. to yield chrysoketone. $MgPhBr$ does not react with (I) at 35°, but in PhMe at 100° gives a small amount of an acidic substance, m.p. 200—210°, and tar containing about 3% of (II). With $Me_2SO_4\cdot NaOH$ (I) gives 7-methoxy-8-phenylperinaphthinden-9-one, m.p. 117—118°, con-

verted by MgPhBr into 7-methoxy-1:8-diphenyl-1:9a-dihydroperinaphthinden-9-one (V), m.p. 152° , which with Me_2SO_4 - NaOH - EtOH affords 1:3-dimethoxy-2:9-diphenylperinaphthindene (VI), m.p. 137° , also obtained from (II).

With LiPh (V) gives only 7-methoxy-1:8-diphenylperinaphthinden-9-one, m.p. 250 – 251° , also obtained by *p*-benzoquinone or, with 7-methoxy-6:8-diphenylperinaphthinden-9-one, m.p. 141 – 142° , by methylating (III). HBr - AcOH hydrolyses the two last-mentioned 7-OMe-ketones to (III), proving that *C*-methylation has not occurred.

R. S. C.

Constitution of the condensation product of diphenylketen and cyclopentadiene. J. R. LEWIS, G. R. RAMAGE, J. L. SIMONSEN, and (in part) W. G. WAINWRIGHT (J.C.S., 1937, 1837–1841).—The ketone prepared by condensation of dimethylketen and cyclopentadiene (cf. Staudinger, A., 1906, i, 234) may be either 6-keto-7:7-dimethyldicyclo[3, 2, 0]hept-2-or -3-ene, and is suggested as a starting point for synthesis of caryophyllenic acid. CPh_2CO and cyclopentadiene yield 6-keto-7:7-diphenyldicyclo[3, 2, 0]hept-2-ene (I), m.p. 86 – 88° . Oxidation of (I) with permanganic acid yields the 2:3-epoxide, m.p. 121 – 122° , which with AcOH - H_2SO_4 gives the 2:3-diacetate, m.p. 122 – 124° , of 2:3-dihydroxy-6-keto-7:7-diphenyldicyclo[3, 2, 0]heptane, m.p. 178 – 180° , alkali fission of which gives the stereoisomeric α -, m.p. 170 – 171° [*Me* ester, m.p. 159 – 160° ; *Et* ester, m.p. 140 – 141° (dibenzoate, m.p. 138 – 139°); *p*-bromophenacyl ester, m.p. 128 – 129°], and β -, m.p. 177 – 180° (*Me* ester, m.p. 126 – 128°), -3:4-dihydroxy-2-benzhydrylcyclopentane-1-carboxylic acids. Oxidation of these acids affords the stereoisomeric α -, decomp. 187 – 188° (*Me* ester, m.p. 117 – 119° ; *Ba* and *Ca* salts) and β -, decomp. 208 – 209° (*Me* ester, m.p. 121 – 122.5°), -4:4-diphenylbutane-1:2:3-tricarboxylic acids, synthesised by condensation of CHPh_2Br and *Me* sodiopropene- $\alpha\beta\gamma$ -tetracarboxylate. The probable configurations of these four acids are discussed. (I) with H_2O_2 undergoes ring fission to an unsaturated lactone, $\text{C}_{19}\text{H}_{16}\text{O}_2$, m.p. 116 – 117° , reduced (H_2 -Pd) to the acid, $\text{C}_{19}\text{H}_{20}\text{O}_2$, probably 2-benzhydrylcyclopentane-1-carboxylic acid, m.p. 125 – 127° .

E. G. B.

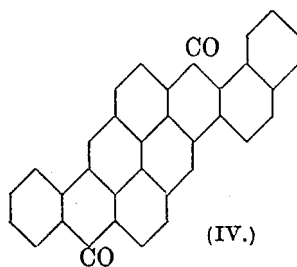
Derivatives of 4-amino-1:2-naphthaquinone. H. GOLDSTEIN and G. GENTON (Helv. Chim. Acta, 1937, 20, 1413–1417).—4-Amino-1:2-naphthaquinone [prep. from 2:4-(NO_2) $_2\text{C}_{10}\text{H}_5\text{OH}$ described] is converted by Ac_2O at 100° into 4-acetamido-1:2-naphthaquinone, incipient decomp. about 220° (corr.). 4:1-NHBz- $\text{C}_{10}\text{H}_6\text{OH}$, m.p. 239° (corr.), is transformed by HNO_2 into the 2-*NO*-derivative (I), m.p. 189° (corr.; decomp.), which gives characteristic colours with FeSO_4 , FeCl_3 , CoCl_2 , NiCl_2 and CuSO_4 . (I) is reduced by SnCl_2 and HCl to 2-amino-4-benzamido-1-naphthol, oxidised by aq. FeCl_3 to 4-benzamido-1:2-naphthaquinone (II), m.p. 245° (corr.; decomp.), the oxime of which is identical with (I). $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$, HCl , and (II) in EtOH at 20° give 6-benzamidonaphthaphenazine, m.p. 274° (corr.).

4-Anilino-1:2-naphthaquinone in EtOH is reduced by SnCl_2 and HCl to 4-anilino-1:2-dihydroxynaphthalene [hydrochloride; diacetate, m.p. 177° (corr.); Ac_3 derivative, m.p. 167° (corr.)]. H. W.

Acenaphthenone and acenaphthenequinone.

H. G. RULE and S. B. THOMSON (J.C.S., 1937, 1761–1763).—Acenaphthenequinone (I) is brominated (liquid Br) to the 3-Br-derivative (monoxime, m.p. 213° – 214.5°). Further bromination in presence of Fe affords 2:3:5(?)-tribromo- (II), m.p. 253 – 256° (phenazine, m.p. 303°), and 2:3:4:5(?)-tetrabromo-, m.p. 300 – 305° , -derivatives. Oxidation of (II) affords a tribromonaphthalic anhydride. The monoxime of (I) undergoes Beckmann transformation on heating into naphthalimide. Acenaphthenone, prepared by reduction of the phenylhydrazone or monoxime of (I), affords the 7:7-Br $_2$ -derivative with excess of Br in CS_2 . 7:7-Dichloroacenaphthenone (III) affords on mild reduction a dinuclear condensation product, 7:7'-diacenaphthylidene-8:8'-dione, further reduced to 7:7'-diacenaphthenonyl, m.p. 258° , also obtained from 7-bromoacenaphthenone by boiling with Cu-bronze. (III) condenses with NH_3 to the dinuclear acenaphthazine, previously obtained from acenaphthenequinone and NH_3 , and with NHMe_2 to *NN'*-dimethyldihydroacenaphthazine. E. G. B.

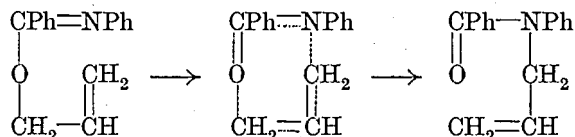
From pyrene to more highly anellated ring systems. R. SCHOLL, K. MEYER, and J. DONAT (Ber., 1937, 70, [B], 2180–2189).—Replacement of CS_2 by C_6H_6 , PhMe , PhCl , or $(\text{CHCl}_2)_2$ and avoidance of a temp. $>20^\circ$ leads to a great improvement in the yield of 3-aryolpyrenes obtained from the aroyl chloride, pyrene (I), and AlCl_3 . The prep. of 3-benzoyl- (II), m.p. 128 – 129° , 3-*p*-bromobenzoyl-, m.p. 174 – 175° , 3-*p*-toluoyl- (III), m.p. 155 – 156° , 3-cinnamyl-, m.p. 119.5 – 120.5° , and 3- α -naphthoyl-, m.p. 153 – 154° , -pyrene is described. 3-Methylpyranthrone is obtained by addition of (II) and $\text{p-C}_6\text{H}_4\text{MeCOCl}$ or of (III) and BzCl to AlCl_3 - NaCl through which O_2 is passing at 110° to 165° . *m*- $\text{C}_6\text{H}_4\text{BrCOCl}$ and (II) give 3-bromopyranthrone, where-



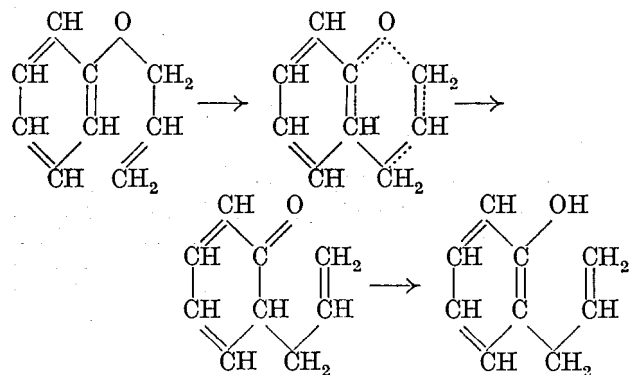
as the yield of dye is very small when *p*- $\text{C}_6\text{H}_4\text{BrCOCl}$ is used. 1- $\text{C}_{10}\text{H}_7\text{COCl}$ and (II) give 1:2-benzopyranthrone (IV) whereas $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$ gives a material of unknown constitution. Interaction of (II) and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ or of *o*-3-pyrenylbenzoic acid and BzCl with AlCl_3 - NaCl gives 2:3-(CO)-benzoylene-8:9- and -9:10-phthaloylpyrene, m.p. 165° . BzCl , (I), and sublimed FeCl_3 in boiling $(\text{CHCl}_2)_2$ give 3:5:8:10-tetrabenzoylpyrene (V), m.p. 278° ; 3:5:8:10-tetra-*o*-chlorobenzoylpyrene, m.p. 359 – 360° (corr.), is obtained similarly. Passage of Cl_2 into (V) suspended in $\text{C}_6\text{H}_3\text{Cl}_3$ at 100° gives 1:2:6:7-tetrachloro-3:5:8:10-tetrabenzoyl-1:2:6:7-tetrahydropyrene, m.p. about 278° (decomp.), which when heated with AlCl_3 - NaCl at 200° gives a mixture of 1:6- and 1:7-dichloro-3:5:8:10-tetrabenzoylpyrene, m.p.

282—300°, and when heated with quinoline and KOH yields 6 : 14-dibenzoylpyranthrone. H. W.

Experiments on the theory of the allyl transformation. O. MUMM and F. MÖLLER (Ber., 1937, 70, [B], 2214—2227).—The allyl transformation is investigated with benzimino allyl ethers since migration of allyl is not here accompanied by wandering of H. It occurs fairly readily and, after migration, the allyl group is attached to N by a C atom different from that by which it was attached previously to O. The course of the change is therefore expressed :



and the transformation of Ph allyl ethers by the scheme :



If both positions *ortho* to the O are occupied, the hydrocarbon residue migrates to the *para* position. In the case of the cinnamyl group the change is "normal" and the group is attached to the ring C by the same C atom as was involved in the previous attachment to O. It remains undecided whether this is a general phenomenon.

Treatment of benzanilide imidochloride (I) with $\text{ONa}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ in C_6H_6 gives *N*-phenylbenzimino allyl ether $\text{NPh}\cdot\text{CPh}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$, b.p. 178.5—181°/14 mm., readily hydrolysed by 1% $\text{HCl}\cdot\text{MeOH}$ to NH_2Ph and allyl benzoate and transformed at 210—215° into benzphenylallylamide, b.p. 196—198°/12—13 mm., identical with that derived from BzCl and allylaniline. Similarly, (I) and Na crotyl oxide afford *N*-phenylbenzimino crotyl ether, b.p. 145—148°/0.5—0.6 mm., readily isomerised to benzphenyl- α -methylallylamide (II), b.p. 194—197°/12 mm.; this is hydrolysed (with addition of H_2O) by boiling conc. HCl to β -hydroxy- α -methylpropylaniline, b.p. 146—147°/13 mm., and BzOH . Hydrogenation (Pd in MeOH) of (II) gives benzphenylsec.-butylamide, b.p. 195—197°/12 mm., hydrolysed with great difficulty by boiling conc. HCl or 50% aq. KOH but transformed by KOH in isoamyl alcohol into sec.-butylaniline, b.p. about 228° (hydrochloride, m.p. 135—136°; *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$ derivative, m.p. 77—78°). NaNH_2 , (I), and methylvinylcarbinol yield *N*-phenylbenzimino α -methylallyl ether, b.p. 129—132°/0.6 mm., isomerised to benzphenylcrotylamide, b.p. 204—207°/13 mm., which is hydrogenated (colloidal Pd) to benzphenyl-*n*-

butylamide, b.p. 202—203.5°/13—14 mm., m.p. 47—48°, hydrolysed to *n*-butylaniline, b.p. about 235° (hydrochloride, m.p. 115°; *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$ derivative, m.p. 47°). Treatment of 2 : 3 : 1- $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{Me}$ with Na and MeOH and then with crotyl bromide affords *Me* 2-crotyloxy-3-methylbenzoate, m.p. 119—122°/0.4 mm. (corresponding acid, m.p. 76°), which passes in boiling NPhEt_2 into *Me* 2-hydroxy-3-methyl-5-crotylbenzoate, b.p. 155—158°/12 mm. The corresponding acid, m.p. 135—136.5°, is decarboxylated in boiling NPhMe_2 to 2-methyl-4-crotylphenol, b.p. 136—139°/12—13 mm., identified by conversion by 33% NaOH and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ into 2-methyl-4-crotylphenoxyacetic acid, m.p. 130—131°; this is oxidised by KMnO_4 in $\text{COMe}_3\cdot\text{H}_2\text{O}$ to 2-methyl-4-carboxyphenoxyacetic acid (III), m.p. 283—284°. Cinnamyl bromide, NaOMe , and 2 : 3 : 1- $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{Me}$ give *Me* 2-cinnamyloxy-*m*-toluate, which becomes isomerised and resinified when distilled in a high vac. and is therefore directly hydrolysed to 2-cinnamyloxy-*m*-toluic acid, m.p. 102—103° [converted when hydrogenated (Pd colloid) into PhPr^a and *o*-hydroxy-toluic acid]. The ester is isomerised in boiling NPhEt_2 and the product is hydrolysed to 2-hydroxy-5-cinnamyl-*m*-toluic acid, m.p. 153°. This when decarboxylated affords 4-cinnamyl-*o*-cresol, m.p. 71—72°, whence 4-cinnamyl-2-methylphenoxyacetic acid, m.p. 123—124°, oxidised by KMnO_4 to (III) and BzOH .

H. W.

Equilibrium of the semiquinone of phenanthrene-3-sulphonate with its dimeric compound.—See A., 1, 13.

Isomerisation of caoutchouc. C. FERRI (Helv. Chim. Acta, 1937, 20, 1393—1395).—Röntgenographic examination of the products of the action of POCl_3 , SnCl_4 , $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, and TiCl_4 on caoutchouc (I) establishes the disappearance of the regular *cis*-chain of (I) and the production of mols. of irregular structure. In consequence of secondary changes isomerisation is only partial and static and in the same chain *cis*- and *trans*-linkings alternate irregularly. This view is confirmed by the similar conversion of guttapercha (II) into a very closely analogous product. In the thermoplastic masses there exists a hydrocarbon intermediate between (I) and (II).

H. W.

Conversion of β -phellandrene into a derivative of α -phellandrene. N. F. GOODWAY and T. F. WEST (Nature, 1937, 140, 934).—Addition of *l*- β -phellandrene to maleic anhydride gives a product apparently identical with the compound obtained (J.S.C.I., 1937, 56, 473 π) from *l*- α -phellandrene.

L. S. T.

(A) Preparation of Δ^1 -dihydroperillyl and tetrahydroperillyl alcohols. (B) Action of oxalic acid on dihydroperillyl and tetrahydroperillyl alcohols. M. A. ISKENDEROV (J. Gen. Chem. Russ., 1937, 7, 1429—1434, 1435—1437).—(A) Perillyl alcohol in MeOH and H_2 (Pd catalyst) yield Δ^1 -dihydro- (I) and tetrahydro-perillyl alcohol (II). The latter yields menthan-7-aldehyde, b.p. 118—119°/20 mm. (semicarbazone, m.p. 112°), when oxidised with CrO_3 .

(B) $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ at 140° converts (I) or (II) into

1-methylene-4- α -methylene-ethyl- or -4-isopropyl-
cyclohexane. R. T.

Syntheses in the thujane group. IV. Synthesis of thujane. P. C. GUHA and S. KRISHNAMURTHY (Ber., 1937, 70, [B], 2112—2117; cf. A., 1937, II, 509).—The following additional compounds are described: 1-methyl-3-isopropyl- Δ^2 -cyclopentene-1-carboxylic acid, m.p. 56°, and its *Et* ester, b.p. 114—115°/11 mm., and dibromide, m.p. 154°. Oxidation of 1-methyl-4-isopropylidicyclo-[0:1:3]-hexane-1-carboxylic acid or of thujane with KMnO_4 gives α -methyl- α' -isopropyladipic acid. H. W.

Syntheses in the camphane series. III. New synthesis of isodehydroapocamphoric acid and Δ^4 -cyclopentene-1:3-dicarboxylic acid. P. C. GUHA and B. K. SANKARAN (Ber., 1937, 70, [B], 2109—2112).—The interaction of Et_2 muconate (I) (improved prep. from adipic acid) and CMe_2N_2 in cold xylene gives Et_2 isodehydroapocamphorate [Et_2 2:2-dimethyl- Δ^4 -cyclopentene-1:3-dicarboxylate], b.p. 200°/100 mm., hydrolysed to isodehydroapocamphoric acid, m.p. 208—209° (anhydride, m.p. 193—195°); addition occurs therefore in the $\alpha\delta$ -position of the conjugated linking. Similarly, (I) and CH_2N_2 afford Et_2 Δ^4 -cyclopentene-1:3-dicarboxylate, b.p. 185—188°/80 mm., hydrolysed to Δ^4 -cyclopentene-1:3-dicarboxylate, m.p. 160—161°, which adds HBr with difficulty and is not reduced by Na or Na-Hg and EtOH . Its constitution is established by its oxidation to glutaric acid. H. W.

Isomeric bornyl mandelates. E. M. LUIS and A. MCKENZIE (Ber., 1937, 70, [B], 2161—2165).—Esterification of (+)-mandelic acid with (+)-borneol and HCl at 100° yields (+)-bornyl (+)-mandelate (I), m.p. 77—78°, $[\alpha]_D^{25} +85.9^\circ$, $[\alpha]_{5461}^{18} +103.1^\circ$ in EtOH . (–)-Bornyl (–)-mandelate (II), m.p. 77—78°, $[\alpha]_D^{25} -85.8^\circ$, $[\alpha]_{5461}^{18} -103.4^\circ$ in EtOH , and (I) when mixed in equal proportions afford optically inactive bornyl mandelate, α -form, m.p. 56—57°. (+)-Bornyl (–)-mandelate (III), m.p. 51—52°, $[\alpha]_D^{25} -23.5^\circ$, $[\alpha]_{5461}^{18} -30.7^\circ$ in EtOH , and (–)-bornyl (+)-mandelate, (IV), m.p. 51—52°, $[\alpha]_D^{25} +23.4^\circ$, $[\alpha]_{5461}^{18} +30.6^\circ$ in EtOH , similarly yield optically inactive bornyl mandelate, γ -form, m.p. 51—52°. Admixture of equal amounts of the α - and γ - gives the β -form, m.p. 32—34°. Compounds are not obtained by admixture of equal amounts of (I) with (IV), (II) with (III), (I) with (III), and (II) with (IV). H. W.

Camphor and terpene series. III. Total synthesis of the santenic acids. G. KOMPPA and W. ROHRMANN. IV. Synthesis of new *cis*- and *trans*-methylsantenic acids. G. KOMPPA, H. PAASIVIRTA, and W. ROHRMANN (Ann. Acad. Sci. fenn., Ser. A., 1935, 44, No. 3, 3—29; No. 10, 3—12; Chem. Zentr., 1936, i, 3838—3840, 3840—3841).—III. Partly an elaboration of work already reported (A., 1933, 70; 1934, 889). The dehydro-santenic acid, m.p. 197—198°, is regarded as $\text{CH}=\text{C}(\text{CO}_2\text{H})\text{CH}:\text{CMe}(\text{CO}_2\text{H}) > \text{CHMe}$ (I) and the acids of m.p. 169—170° (IIa) and 148° (IIb) as stereoisomerides of $\text{CH}_2=\text{C}(\text{CO}_2\text{H})\text{CH}:\text{CMe} > \text{CMe}$. $\text{Me}_2\text{C}_2\text{O}_4$ and Me_2 β -methyl-

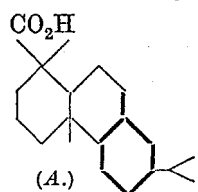
glutarate yield Me_2 4:5-diketo-2-methylcyclopentane-1:3-dicarboxylate, m.p. 103—104°, (phenylosazone, decomp. 159°; phenylosazone of corresponding Et_2 ester, m.p. 117—118°), which is methylated (MeI-NaOMe) to Me_2 4:5-diketo-1:2-dimethylcyclopentane-1:3-dicarboxylate (III), m.p. 54—55° (phenylosazone, m.p. 161—162°), accompanied by Me_2 5-keto-4-methoxy-1:2-dimethyl- Δ^3 -cyclopentene-1:3-dicarboxylate, b.p. 177—178°/10 mm. (corresponding Et_2 ester, b.p. 172—173°/10 mm.). (III) with Na-Hg in Na_2CO_3 , followed by HI and red P , yields a dehydrosantenic acid (I), m.p. 197—198°, which is hydrogenated (Pt) to *cis*-isosantenic acid (IV), m.p. 151—152° (anhydride, m.p. 93—94°; anilic acid, m.p. 211—211.5°; anil, m.p. 129—130°). Bromination, followed by elimination of HBr , yields (IIa). With AcOH-HCl (IV) yields *trans*-isosantenic acid, m.p. 129—130°; similarly *cis*-santenic acid (anilic acid, m.p. 205—206°; anil, m.p. 117—118°; Et_2 ester, b.p. 143—144°/14 mm.) yields *trans*-santenic acid, m.p. 164—165° (dianilide, m.p. 221°). Et_2 α -bromosantenate, b.p. 157.5—158°/11 mm., with EtOH-KOH , yields (IIa), together with some hydroxy-santenic acid and the corresponding lactonic acid, m.p. 137°, whereas boiling quinoline yields the Et_2 ester, b.p. 149°/14 mm., of (IIb). Santenimide, m.p. 138—139°, with NaOH yields 1-amino-1:2-dimethylcyclopentane-3-carboxylic acid, m.p. >250°, and with NaOH , α -santenamic acid, m.p. 192.5—193°.

IV. Et 2-cyano-2:5-dimethylcyclopentanone-5-carboxylate with MeMgI yields Et 2-hydroxy-3-cyano-1:2:3-trimethylcyclopentane-1-carboxylate, b.p. 110—125°/0.4 mm., dehydrated ($\text{NaSO}_4\text{-Na}_2\text{S}_2\text{O}_7$) and hydrolysed (KOH) to a mixture of two dehydromethylsantenic acids, m.p. 197—198° and m.p. 238—239°. The former is hydrogenated (Pd-Pt) to *cis*-, m.p. 189° (anhydride, m.p. 93—94°), and the latter to *trans*-, m.p. 244—245°, methylsantenic acid. H. N. R.

Catalytic hydrogenation of azines. VI. Comparison of velocity of hydrogenation of camphor and carvomenthone ketazines. K. A. TAIFALE, M. A. GUTNER, and E. K. REMIZ (J. Gen. Chem. Russ., 1937, 7, 1378—1389).—The velocity of hydrogenation of camphor ketazine (I) in AcOH (Pt catalyst at room temp.) is $\frac{1}{4}$ that of carvomenthone ketazine. The sole product thus obtained from (I) is 2-hydrazocamphane, m.p. 135—136° [hydrochloride, m.p. 235° (decomp.); Bz_1 derivative, m.p. 137—138°], oxidised by KMnO_4 to 2-azocamphane, m.p. 148—149° (decomp.), $[\alpha]_D^{25} -59.44^\circ$ in C_6H_6 , which with HCl gives *N*-bornyl-*N'*-bornylidenedehydrazine hydrochloride, m.p. 200° (decomp.). This is hydrolysed by 30% HCl to bornylhydrazine and camphor. R. T.

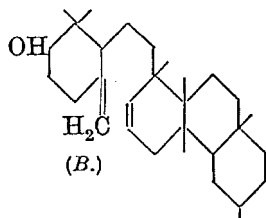
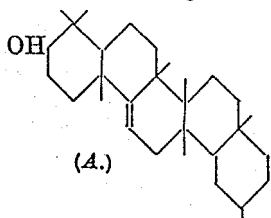
isoFenchone. I. isoFenchone-, isofenchol-, and fenchylene-carboxylic acids. A. K. RUSHEN-CEVA (J. Gen. Chem. Russ., 1937, 7, 1343—1351).—isoFenchocarboxylic acid is reduced electrolytically to yield a mixture of stereoisomeric hydroxy-acids, converted by HNO_3 into isofenchone, and by AcCl into a mixture of the acetate, m.p. 129.5—130.5°, of isofencholcarboxylic acid, m.p. 134—135°, with its anhydride, and with a lactone (not isolated); this mixture yields fenchylenecarboxylic acid, m.p. 86—87°, when distilled at 130—160°/10 mm. R. T.

Polyterpenes and polyterpenoids. CXIX. Number and relative position of the double linkings in *l*-pimaric acid. L. RUZICKA and R. G. R. BACON [with S. KUIPER] (Helv. Chim. Acta, 1937, 20, 1542—1552).—Evidence is adduced in favour of the view that *l*-pimaric acid (I) contains only two double linkings which are in conjugation, that the phenanthrene ring is present in it, and, from spectroscopic evidence, that the double linkings in abietic acid (II) are isolated. The mol. refraction of *Me l*-pimarate, m.p. 63—64°, $[\alpha]_D -268^\circ$ in Et₂O, obtained from (I) and CH₂N₂ or from the Ag salt and MeI, is exactly that required by the presence of two double linkings. Hydrogenation (Adams-Shriner) of (I) in EtOH gives a mixture of substances from which *l*-dihydropimaric acid (III), m.p. 135—136°, $[\alpha]_D +35^\circ$ in EtOH, is isolated; its *Me* ester, m.p. 88°, has one double linking. Hydrogenation (PtO₂) of (III) gives a mixture which does not give a colour with C(NO₂)₄ and from which *l*-tetrahydropimaric acid (IV), m.p. 195—197°, $[\alpha]_D +7^\circ$ in EtOH, is isolated; its *Me* ester, m.p. 76—77°, $[\alpha]_D +3^\circ$ in EtOH, is spectroscopically a tricyclic, saturated compound. Maleic anhydride (V) and (I) in C₆H₆ at room temp. give quantitatively the same adduct



as is obtained from (II) at higher temp. The product is undoubtedly derived from (I); hence at >100° (II) is in equilibrium with a small proportion of (I). For the double linkings of (II) only the accentuated linkings in A can be considered. The double linkings of (I) must lie in the lowest 6-membered ring. Attempts to use (V) for the determination of (I) in pine resin show the presence of only about one third the amount present in galipot. Retene is obtained in good yield by the dehydrogenation of di- and tetra-hydroabietic acid, (III) and (IV) by Pd-C at 320—330°. H. W.

Polyterpenes and polyterpenoids. CXX. Transformation of oleanolic acid into β -amyrin and erythrodiol. L. RUZICKA and H. SCHELLENBERG (Helv. Chim. Acta, 1937, 20, 1553—1556).—Acetyloleanolic acid is transformed by SOCl₂ into the chloride, m.p. 226—228° (decomp.), converted by Rosenmund's method into the corresponding aldehyde, m.p. 227—229° after slight softening [oxime, m.p. 190—200° (much decomp.); semicarbazone (I), m.p. 240—250° (decomp.)]. NaOEt in EtOH at 200° converts (I) into a mixture of β -amyrin (II), m.p. 198—199°, $[\alpha]_D +88.6^\circ$ in CHCl₃ (acetate, m.p. 240—241°, $[\alpha]_D +81.0^\circ$ in CHCl₃; benzoate, m.p. 234—235°), and erythrodiol, m.p. 232—233°, $[\alpha]_D +74.6^\circ$ in CHCl₃ (diacetate, m.p. 184—185°, $[\alpha]_D$

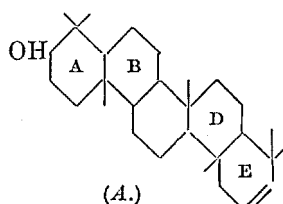


+60.0° in CHCl₃), separated from one another by adsorption by Al₂O₃ and fractional elution. Based

on the structure of oleanolic acid, (II) and basseol have the constitutions A and B, respectively.

H. W.

Polyterpenes and polyterpenoids. CXXI. Empirical formula and dehydrogenation of lupeol. L. RUZICKA, M. FURTER, P. PIETH, and H. SCHELLENBERG (Helv. Chim. Acta, 1937, 20, 1564—1570).—Elementary analysis of lupeol (I) does not distinguish between the homologous formulae C₃₀H₅₀O \pm CH₂. Therefore (I) is transformed into its



tribromoacetate, m.p. 225°, analyses of which establish the presence of 32 C and hence of 30 C in (I). The presence of a double linking in (I), indicated by the colour with C(NO₂)₄ (with which dihydrolupeol does not react), is confirmed by the mol. refraction. Hence (I) is a pentacyclic triterpene. Dehydrogenation of (I) with Se at 350° gives 1 : 2 : 5-C₁₀H₅Me₃ and 1 : 2 : 5 : 6-C₁₀H₄Me₃·OH; a homologue of picene could not be isolated. The structure A is suggested for (I).

H. W.

Polyterpenes and polyterpenoids. CXXII. Detection of a double linking in quinovic acid.

L. RUZICKA and V. PRELOG (Helv. Chim. Acta, 1937, 20, 1570—1575).—Me₂ quinovate, m.p. 175—176°, and its Ac derivative (I), m.p. 218—219°, give a marked yellow colour with C(NO₂)₄ in CHCl₃ and since these compounds are transformed by 30% KOH-EtOH at 150° into quinovic acid (II) it also contains a double linking. This view is confirmed by the observation that the product of the oxidation of (I) by CrO₃ in an α -unsaturated ketone (spectrochemical proof), reduced (PtO₂ in AcOH) to a compound, m.p. 218—219°, containing 2H in place of O. Pyroquinovic acid and (II) are therefore A with R = H and R = CO₂H, respectively.

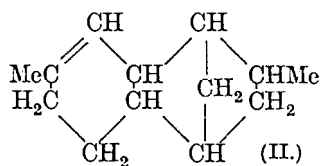
H. W.

Alkaline degradation of pine wood. III. R. S. HILPERT and W. HANSI (Ber., 1937, 70, [B], 2209—2214; cf. A., 1937, II, 205).—The proportion of pine wood dissolved by conc. aq. NaOH depends exclusively on the ratio H₂O : NaOH and is independent of the time. Under the most drastic conditions only 8% of the wood remains; the result is unaffected by the presence of CS₂. The amount of material pptd. by acids from the alkaline solution diminishes as the concn. of the alkali increases. The solution still contains products of high mol. wt. which are pptd. by NaCl. The elementary composition of the ppts. is the same as that of the wood; OMe varies progressively. When the ppts. are worked up for lignin certain not very marked differences from the behaviour of unchanged wood are observed. Further acidification of the liquid above the ppts. causes darkening of colour and separation of small amounts of solid which is re-dissolved when the mixture is diluted with H₂O and neutralised.

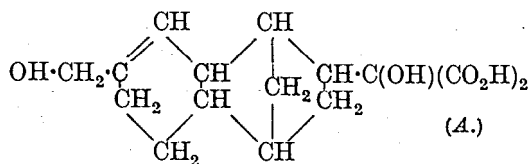
This behaviour is not due to the presence of large amounts of salts. Acidification of the alkaline wood solutions with AcOH and treatment with $\text{Hg}(\text{OAc})_2$ does not cause pptn., so that phenols with or without side chains are not present. The experiments support further the hypothesis that the so-called "lignin" is not a component of wood but is a reaction product in which the presence of large amounts of aromatic groups is very improbable. Similarly since wood can be dissolved almost completely by sufficiently conc. alkali it follows that the wood gum or hemicelluloses are merely reaction products the formation of which is conditioned by the previously accidentally chosen conditions of reaction. H. W.

Convallotoxin. L. F. FIESER and R. P. JACOBSEN (J. Amer. Chem. Soc., 1937, 59, 2335—2339).—Alcoholysis of convallotoxin (I) gives oxidodianhydrostrophanthidin methylal and the crude product gives di- and tri-anhydrostrophanthidin. Tschesche reports that the anhydroaglucone benzoate is identical with anhydrostrophanthidin benzoate. Thus (I) is a glucoside (? rhamnoside) of strophanthidin. Its greater activity compared with cymarins is another example of the effect of the sugar. R. S. C.

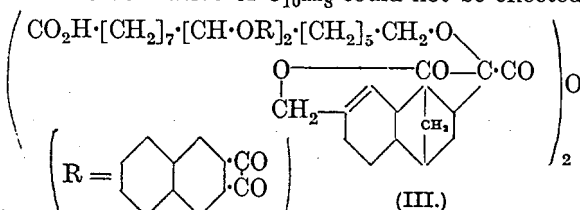
Shellac. XI. Constitution of shellolic acid. W. NAGEL and W. W. MERTENS (Ber., 1937, 70, [B], 2173—2179).—The finely powdered shellac is extracted with Et_2O and aleuritic acid is pptd. as the K salt by contact with 5N aq. KOH for 24 hr. The filtrate is acidified with H_2SO_4 and the resin acids are removed by Et_2O and then converted into their Ba salts, which are purified by adsorption with BaCO_3 . The sol. Ba salts are decomposed with dil. H_2SO_4 , and the acids are removed with Et_2O and esterified with HCl-MeOH . Me_2 shellolate is crystallised from EtOAc and then hydrolysed by $\text{N-H}_2\text{SO}_4$, thus giving shellolic (dihydroxy-shellenedicarboxylic) acid (I) with certainty. The acid is too unstable to permit dehydrogenation by the usual methods but treatment with HI ($d\ 1.7$) and red P at 160° leads to the fundamental hydrocarbon shellane (II), b.p. $146^\circ/748\text{ mm.}$,



with HI ($d\ 1.7$) and red P at 160° leads to the fundamental hydrocarbon shellane (II), b.p. $146^\circ/748\text{ mm.}$,



which is pronouncedly unsaturated; its conversion into a true derivative of C_{10}H_8 could not be effected.



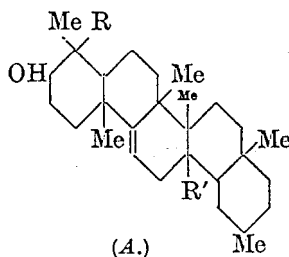
Probably (I) is A in which the position of the two OH is somewhat uncertain. Br and NaHCO_3 transform

(I) into a monobasic acid, $\text{C}_{15}\text{H}_{10}\text{O}_6\text{Br}$, m.p. 226° (also monohydrate, m.p. $125-128^\circ$ after softening), which is probably a Br-lactone. Formula (III) is assigned to shellac. H. W.

Soya-bean saponins. I. E. OCHIAI, K. TSUDA, and S. KITAGAWA (Ber., 1937, 70, [B], 2083—2092).—Extraction of the crude Ca salt of the saponin with hot 80% MeOH removes genistin, $\text{C}_{21}\text{H}_{20}\text{O}_{10}$, decomp. 250° (acetate, m.p. 187°), hydrolysed to genistein, m.p. $298-300^\circ$. The cryst. residue, decomp. 272° , is transformed by HCl into the saponin, $\text{C}_{40}\text{H}_{32}\text{O}_{20}$ or $\text{C}_{48}\text{H}_{32}\text{O}_{19}$, decomp. 222° . This is hydrolysed to a mixture of saponins which form mixed crystals and are separated from one another by a combination of crystallisation and chromatographic analysis. Thus are obtained: soya-sapogenol A (I), m.p. $308-312^\circ$, $[\alpha]_D^{25} +102.3^\circ$ in CHCl_3 ; soya-sapogenol B (II), $\text{C}_{30}\text{H}_{50}\text{O}_3$, m.p. $258-259^\circ$, $[\alpha]_D^{30.5} +92.4^\circ$ in CHCl_3 (triacetate, m.p. $175-176^\circ$; tri-p-bromobenzoate, m.p. $255-257^\circ$; acetate dibromide m.p. $225-227^\circ$, and another bromide), in which the presence of a double linking is established by BzO_2H but not by hydrogenation (PtO_2): soya-sapogenol C (III), $\text{C}_{30}\text{H}_{50}\text{O}_2$, m.p. $238-239^\circ$, $[\alpha]_D^{31} +70.7^\circ$ in CHCl_3 (acetate, m.p. 198° ; dibenzoate, m.p. 188° ; acetate dibromide, m.p. $225-227^\circ$), hydrogenated (PtO_2) to dihydrosoya-sapogenol C, m.p. $243-245^\circ$ (diacetate, m.p. 188°); soya-sapogenol D (IV), $\text{C}_{30}\text{H}_{50}\text{O}_3$, m.p. $298-299^\circ$, $[\alpha]_D^{31} -60.77^\circ$ in CHCl_3 (acetate, m.p. 192° ; benzoate, m.p. 240°). Treatment of (I) with 5% H_2SO_4 -aq. EtOH gives a substance, m.p. $225-228^\circ$. The soya-sapogenols A, B, and C of Miyasaka (J. Pharm. Soc. Japan, 1937, 57, 98) appear identical with (I), (II), and (III) and with glycigenol M^4 , M^2 , and M^1 of Nozoye and Katsura (J. Chem. Soc. Japan, 1937, 58, 570) whilst (IV) appears identical with glycigenol M^3 . H. W.

Soya-bean saponins. II. Dehydrogenation of soya-sapogenol B by selenium. E. OCHIAI, K. TSUDA, and S. KITAGAWA (Ber., 1937, 70, [B], 2093—2096).—Dehydrogenation of soya-sapogenol B (I) in comparison with cholesterol (II) by Se at $330-350^\circ$ for 4 hr. gives mobile fractions from (I) which are not derived from (II). These fractions contain sapotalin, a tetramethylnaphthalene (picrate, m.p. 134°), a hydrocarbon $\text{C}_{27}\text{H}_{28}$ (picrate, m.p. 198°) apparently identical with that derived from sumaresinolic (III) and siaresinolic acid (IV), but nothing corresponding with methylcyclopentenophenanthrene. Prolongation of the period of dehydrogenation yields also (?) a homologous picene identical with that derived from hederagenin, (III), (IV), and panaxsaponin. Since the four soya-sapogenols differ from one another only in the no. of O atoms they all probably have the C skeleton A. H. W.

Amyrins. H. DIETERLE, H. BRASS, and F. SCHAAL (Arch. Pharm., 1937, 275, 557—570).—An improved separation of α - and β -amyrin benzoate is achieved by gradually adding EtOAc to the hot



solution of the mixture in C_6H_6 , whereby the β -compound is pptd. α -Amyren (I) is transformed by successive treatments with CH_3Bu^tOK , CS_2 , and MeI into its *methylxanthate*, $C_{32}H_{52}OS_2$, m.p. 218°; the corresponding β -compound has m.p. 218°. When heated somewhat above their m.p. these compounds afford the corresponding amyrenes, which are less contaminated with resinous products than when formed from the benzoates. Oxidation of (I) with CrO_3 in $AcOH$ at room temp. and purification of the product by distillation in a high vac. gives homogeneous α -amyrene (II), $C_{30}H_{48}O$, m.p. 126° (*dinitrophenylhydrazone*, m.p. 218°), and a *ketone*, $C_{21}H_{34}O$, m.p. 158° [*oxime*, m.p. 219° (decomp.)]. α -Amyren-oxime (III), m.p. 235°, is unchanged by attempted hydrogenation in presence of colloidal Pt (Skita) but is transformed (PtO_2 in $AcOH$) into *amyramine*, $C_{30}H_{51}N$, m.p. 140° (*picrate*, decomp. 220°; *platnichloride*). This yields only amorphous, resinous materials when dry-distilled. Treatment of (III) with H_2 at 100°/45 atm. (Ni) gives NH_3 and (II) but no amine. Further oxidation of (II) by CrO_3 in $AcOH$ gives a neutral compound, $C_{21}H_{34}O$, m.p. 230°, in which the function of the O could not be established, and a dibasic acid, $C_{22}H_{32}(CO_2H)_2$ (Me_2 ester, m.p. 249–250°). Oxidation of β -amyren acetate by CrO_3 in $AcOH$ at 95° gives β -hydroxyamyren acetate (IV), m.p. 293°, $[\alpha]_D^{25} +2.5^\circ$ in C_6H_6 , and β -hydroxyisoamyren acetate, m.p. 253°, $[\alpha]_D^{25} +61.1^\circ$ in C_6H_6 . These are hydrolysed to β -hydroxyamyren, m.p. 207°, and β -hydroxyisoamyren, m.p. 222–223°, respectively. Attempted fission of the assumed ethylene oxide ring by treatment of (IV) with conc. HCl at 140° yields a substance, $C_{30}H_{48}O$ or $C_{30}H_{46}O$, m.p. 173.5–174°, which does not decolorize $KMnO_4$ or Br or give a yellow colour with $C(NO_2)_4$ and in which O does not appear to be present as OH or CO . Gradual addition of CrO_3 to (IV) in boiling $AcOH$ affords the dibasic β -amyranthreic acid, $C_{18}H_{30}(CO_2H)_2$, decomp. 304–305° after softening at 300° [Me_2 ester, m.p. 184–185°; *anhydride*, m.p. 310–311° (decomp.)], and a neutral compound, $C_{20}H_{30}O_3$, m.p. 310–311° (decomp.). Attempts to secure intermediate products of the oxidation of (IV) by use of SeO_2 or $KMnO_4$ were unsuccessful, unchanged materials and resins resulting. In the prep. of amyrenes according to Vesterberg the duration of the change is an important factor since the initial product amyren I (V), m.p. 173–177°, $[\alpha]_D^{25} +712^\circ$, gradually passes under the influence of the liberated HCl into amyren III, $C_{30}H_{48}$, m.p. 103°, $[\alpha]_D^{25} +155^\circ$ in C_6H_6 . The indefinite m.p. of (V) is not due to the presence of a mixture of isomerides. Treatment of (I) with p - $C_6H_4MeSO_2Cl$ and C_5H_5N at 100° gives amyren II, $C_{30}H_{48}$, m.p. 147–148°.

H. W.

Cork. VIII. Cork wax. F. ZETSCHE and E. LÜSCHER (J. pr. Chem., 1937, [ii], 150, 68–80).—The wax is extracted by $EtOH-C_6H_6$ from cork powder and boiled successively with aq. Na_2SO_3 , 1% HCl , and H_2O . Hydrolysis with $KOH-EtOH$ gives about 26% of acidic and 74% of non-acidic components. The former include linoleic, oleic, cerotic, arachic, α -hydroxyarachic, and phellonic acids and an acid $C_{30}H_{48}O_3$ [$+MeOH$, m.p. 295° in an open, 302° in a sealed, capillary; Me ester, m.p. 209° after

softening at 200°; *Br-lactone*, $C_{20}H_{47}OBr$, m.p. 234–236° (decomp.)], probably identical with oleanolic acid. Resin acids which could not be separated into individual components and a mixture of fatty acids, mainly stearic acid, are also found. The non-acidic compounds comprise the *alcohols*, $C_{21}H_{44}O$, m.p. 71° (*acetate*, m.p. 48°), and $C_{24}H_{42}O_2$, m.p. 245–246° (*acetate*, m.p. 214–216°; *Br-derivative*, $C_{24}H_{41}O_2Br$, m.p. 114°), identical with the substance obtained by Zellner from the bark wax of *Platanus orientalis*, Hesse's phytosterol mixture, cerin (I), and friedelin (II), and a vaseline-like mixture of the mean composition $C_{18}H_{30}O$ in which alcohols are present. The acids identified in (I) and (II) up to eicosanedicarboxylic acid are saturated and unsaturated hydroxy-mono- and -di-carboxylic acids; phlorone, phloronic, suberic, suberolic, cutic, cutinic, and phellonic acid. The acid $C_{30}H_{48}O_3$, (I), (II), and alcohols $C_{21}H_{44}O$ and $C_{24}H_{42}O_2$ appear to be derived from the actual wax. It is very improbable that cutin and suberin are secondary products of the allied cuticular wax; they are better regarded as sp. degradation products of the plant organism. They and wax are not formed the one from the other but one with the other whereby many intermediates are probably common to both. Cork wax does not appear to differ fundamentally from other bark waxes.

H. W.

Shikimic acid and derivatives. I. Salts of shikimic acid. H. H. LEI (J. Amer. Pharm. Assoc., 1937, 26, 900–902).—The *Li*, *Ag*, *Cu*, *Zn*, *Na*, *K*, *Mg*, *Ca*, *Sr*, *Ba*, and *Pb* salts were prepared (cf. Chen, A., 1930, 259).

F. O. H.

Hydrogenation of furan and its alkyl derivatives in presence of palladium catalysts. N. I. SCHUJIKIN, V. I. NIKIFOROV, and P. A. SMOLIAROVA (J. Gen. Chem. Russ., 1937, 7, 1501–1506).—The products of hydrogenation of furan derivatives at 150° (Pd -asbestos catalyst) are always tetrahydroderivatives. The velocity of hydrogenation falls in the order furan > 2-methyl- > 2-ethyl- > 2:5-dimethyl-furan.

R. T.

4-Chloro-3-acetoxy-2:5-diphenylfuran. R. E. LUTZ, A. H. STUART, F. N. WILDER, and W. C. CONNOR (J. Amer. Chem. Soc., 1937, 59, 2314–2315).—*cis*-(but not *trans*)- $CHBz:CClBz$ or $OH:CHBz:CHClBz$ with $H_2SO_4-Ac_2O$ gives 4-chloro-3-acetoxy-4:5-diphenylfuran, m.p. 119°; the *cis*-compound with warm $AcCl$ and a drop of H_2SO_4 gives 3:4-dichloro-4:5-diphenylfuran. Previous results are corr. R. S. C.

2-Hydroxy-3-keto-2:5-diphenyl-4-methyl-2:3-dihydrofuran. R. E. LUTZ and A. H. STUART (J. Amer. Chem. Soc., 1937, 59, 2316–2321).—2-Hydroxy-3-keto-2:5-diphenyl-4-methyl-2:3-dihydrofuran (I), like the tri- but unlike the di-phenyl analogue, reacts as a cyclic compound exclusively. Two of three attempted syntheses of (I) from mesaconic anhydride failed. $CHBz:CMcBz$ (II) with $AcCl-H_2SO_4$ gives 3-chloro-, m.p. 82–82.5°, and with $H_2O_2-HBr-Ac_2O-H_2SO_4$ gives 3-bromo-2:5-diphenyl-4-methylfuran (III), m.p. 73.5°, converted by HNO_3-AcOH into β -bromo- $\alpha\delta$ -diphenyl- γ -methyl- Δ^8 -butene- $\alpha\gamma$ -dione, m.p. 85° [reduced by $Zn-AcOH$ to (II)];

with NaOMe (III) gives impure α -methoxy- $\alpha\delta$ -diphenyl- Δ^8 -butene- $\alpha\delta$ -dione, which with O_3 affords BzOH and BzCO₂H, and is hydrolysed to (I) by dil. acid. O_3 converts (I) into BzOH (1.66 mols.) and BzCO₂H (0.1 mol.). The Ag salt of (I) is unstable. Methylation of (I) by various methods gives the 2-OMe-compound, m.p. 67—68°, which with O_3 gives BzOH and BzOMe, is readily hydrolysed to (I), and with HCl-EtOH gives the 2-OEt-compound, m.p. 90—90.5°, also obtained from (I). With AcCl-H₂SO₄ or, less well, with BzCl-H₂SO₄ or SOCl₂ (I) gives 2-chloro-3-keto-2:5-diphenyl-4-methyl-2:3-dihydrofuran (IV), m.p. 68—69°, which with *o*-C₆H₄(NH₂)₂ gives 3-phenyl-2- α -benzoylthylquinoxaline (V), m.p. 155.5—156°, oxidised by CrO₃ to BzOH, 2-acetyl-3-phenylquinoxaline, new m.p. 110—111°, and a little 2-hydroxy-3-phenylquinoxaline (also obtained from the 2-Ac derivative by CrO₃). 3-Keto-2-benzoyloxy-2:5-diphenyl-4-methyl-2:3-dihydrofuran, m.p. 167°, is obtained from (I), Bz₂O, and a trace of H₂SO₄, or, less well, from BzCl with (I) in NaOH or the Na derivative of (I) in Pr²O, or from (IV) and AgOBz in Pr²O; it is rapidly hydrolysed by cold NaOMe. With Ac₂O-H₂SO₄ (I) gives the acetate, m.p. 168—169°, which is readily hydrolysed. With *o*-C₆H₄(NH₂)₂ (IV) rapidly gives (V), and with Zn dust in AcOH at 100° gives 3:3'-diketo-2:5:2':5'-tetraphenyl-4:4'-dimethyl-2:3:2':3'-tetrahydro-2:2'-difuryl, m.p. 283—285°, obtained also from (IV) by H₂-Pd-BaSO₄ or, best, by Cu-bronze in C₆H₆. 2-Hydroxy-3-keto-2:4:5-triphenyl-2:3-dihydrofuran, m.p. 187—189°, gives a Ag derivative, which with MeI gives the 2-OMe-compound. With Br in CHCl₃ or EtOH (I) gives γ -bromo- $\alpha\delta$ -diphenyl- γ -methylbutane- $\alpha\beta\gamma$ -trione, m.p. 95°, which regenerates (I) with Na₂S₂O₄ and with HCl-MeOH gives β -bromo- $\gamma\gamma$ -dimethoxy- $\alpha\delta$ -diphenyl- β -methylbutane- $\alpha\delta$ -dione, m.p. 144°, readily hydrolysed to the triketone by acid. M.p. are corr. R. S. C.

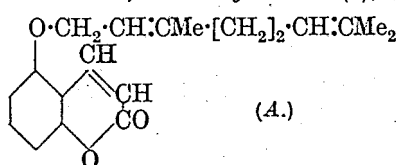
Halogen derivatives of $\alpha\delta$ -diphenylbutane- $\alpha\beta\delta$ -trione and 2-hydroxy-3-keto-2:5-diphenyl-2:3-dihydrofuran. R. E. LUTZ and A. H. STUART (J. Amer. Chem. Soc., 1937, 59, 2322—2326).—Bromination stabilises the ketonic ring-form of 2-hydroxy-3-keto-2:5-diphenyl-2:3-dihydrofuran (I), but does not entirely suppress its reaction in the enolic form. With Br in CHCl₃ or CCl₄ at 0° (I) gives the 4-Br-derivative (II), m.p. 128—130°, which gives no FeCl₃ colour, is unchanged by dissolution in alkali, is unaffected by hot EtOH, SO₂ in dioxan, Me₂SO₄ and alkali, Zn-AcOH, or Br-CHCl₃, but with Br in EtOH gives $\gamma\gamma$ -dibromo- $\alpha\delta$ -diphenylbutane- $\alpha\beta\delta$ -trione (III), m.p. 107.5°. KI does not react with (II) in AcOH, but liberates I almost quantitatively in acidified EtOH. The enolic form (IV) of $\alpha\delta$ -diphenylbutane- $\alpha\beta\delta$ -trione with Cl₂-CHCl₃ gives the Cl-analogue, m.p. 148°, of (II), and with I-CHCl₃ gives the I-analogue, m.p. 124°, also obtained from the Na enolate or from (II). Alcoholic HCl readily gives 4-bromo- (V), m.p. 78°, and 4-chloro-3-keto-2-methoxy-2:5-diphenyl-2:3-dihydrofuran, m.p. 64—65°, and 4-bromo-3-keto-2-ethoxy-2:5-diphenyl-2:3-dihydrofuran, m.p. 95°, which are readily hydrolysed. With AcCl-H₂SO₄ (II) gives 2-chloro-4-bromo-3-keto-2:5-diphenyl-2:3-dihydrofuran, m.p. 106.5°, and with Ac₂O-H₂SO₄ the

2-OAc-analogue, m.p. 184.5° (readily hydrolysed). With *o*-C₆H₄(NH₂)₂ (II) gives 2- α -bromophenacyl-3-phenylquinoxaline, m.p. 191—192°. With CH₂N₂ in Et₂O at 0° (II) gives β -bromo- γ -methoxy- $\alpha\delta$ -diphenyl- Δ^8 -butene- $\alpha\delta$ -dione, m.p. 88°, reduced by Zn-AcOH to 3-methoxy-2:5-diphenylfuran. The yellow Ag salt of (II) with MeI in Et₂O suffers C-methylation to give COPh.CMeBr.CO-COPh and O-methylation to yield (V). Bromination of (IV) gives (III) and prolonged chlorination gives $\gamma\gamma$ -dichloro- $\alpha\delta$ -diphenylbutane- $\alpha\beta\delta$ -trione, m.p. 66.5° (also obtained from the Cl₁-furan); I is liberated quantitatively from KI by (III) in acidified EtOH, but only partly in AcOH; the bromoquinoxaline is obtained from (III). The Cl₂-compound liberates I quantitatively in AcOH. The Na derivative of (II) or its Cl-analogue yields γ -chloro- γ -bromo- $\alpha\delta$ -diphenylbutane- $\alpha\gamma\delta$ -trione, m.p. 96—97°, from which the Br is removed by KI. Both (I) and (IV) titrate (Kurt Meyer) as 100% enol with Br, as HBr catalyses the equilibration; if an excess of C₁₀H₇.OH is used, it is brominated by the Br-ketone formed. M.p. are corr. R. S. C.

Heteropolarity. XXXI. Products of the oxidation of tetracyclone. R. PÜTTER and W. DILTHEY (J. pr. Chem., 1937, [ii], 150, 40—44; cf. A., 1937, II, 463).—Benzoin is converted by CH₂Ph.COCl at 100° into its phenylacetate, m.p. 71°, transformed by NaNH₂ in Et₂O into 2-hydroxy-3:4:5-triphenylfuran (I), m.p. 125°, the structure of which is established by its conversion by CH₂Ph.MgCl into 3:4:5-triphenyl-2-benzylfuran (II), m.p. 163°. (I) is identical with the degradation products of dihydroxy-tetracyclone (which is therefore probably A) and (II) with the substance obtained by hydrogenation (Pd) of tetracyclone hydrate. H. W.

Reactivity of the double linking in coumarins and related $\alpha\beta$ -unsaturated carbonyl compounds. IV. Action of bromine on coumaric acids. P. S. RAO and T. R. SESHADRI (Proc. Indian Acad. Sci., 1937, 6, A, 238—242).—Bromination in boiling AcOH of coumaric, 4-methyl- and 5-nitro-coumaric acids, and decomp. of the crude dibromide with cold EtOH-KOH, or by repeated crystallisation, yields 3:6:8-tribromo-, 3:6:8-tribromo-7-methyl-, and 3:8-dibromo-6-nitro-coumarin, respectively, with small amounts of less brominated products. A. LI.

Natural coumarins. XXXIV. Bergamottin and the detection of limettin in oil of bergamot. E. SPÄTH and P. KAINRATH (Ber., 1937, 70, [B], 2272—2276).—Application to bergamot oil of the author's method of isolating the non-phenolic constituents leads to the identification of bergapten, limettin, m.p. 146—147°, and bergamottin (I), m.p. 59—61°, which



may be identical with the bergapten of von Soden and Rojahn. (I) is optically inactive and free from OMe. At 180—190°/1 mm., (I) is decomposed into bergapten (II). Treatment of (I) with AcOH at 115—120° gives (II) and a

$C_{10}H_8Br \cdot OH$. The inclined form of both $C_{10}H_8$ nuclei is therefore established in this case. Since this compound is readily transformed into *ms*-phenyldibenzoxanthan identical with that derived from $PhCHO$ and β - $C_{10}H_7 \cdot OH$, the inclined form of the $C_{10}H_8$ nuclei is again proved. H. W.

Unsaturated sulphones. I. Preparation, constitution, and tautomerism of sulphones. E. DE R. VAN ZUYDEWIJN (Rec. trav. chim., 1937, **56**, 1047—1062).—3-Methyl- Δ^3 -thiacyclopentene 1:1-dioxide in aq. KOH in the dark is partly transformed into the Δ^2 -compound, m.p. 77.5—78°, which with O_3 in aq. $CHCl_3$ yields β -acetylsulphonic acid (*Ba* salt), oxidised (KOB) to β -sulphopropionic acid (I) (*Ba* salt). Similarly Δ^3 -thiacyclopentene 1:1-dioxide in KOH in ultra-violet light yields Δ^2 -thiacyclopentene 1:1-dioxide b.p. 106—108°/ $<10^{-2}$ mm., m.p. 48.5—49.5° [oxidised by O_3 in $CHCl_3$ to (I)], and 3-hydroxythiacyclopentene 1:1-dioxide, b.p. 140—144°/ $<10^{-2}$ mm., m.p. about 35° (acetate, m.p. 74—75.5°). 3:4-Dimethyl- Δ^3 -thiacyclopentene 1:1-dioxide undergoes no isomerisation with KOH-EtOH or $NaOPr^E$ -EtOH in ultra-violet light. α -Benzylsulphonyl- Δ^2 -propene similarly treated yields α -benzylsulphonyl- β -hydroxypropane, whilst α -di(benzylsulphonyl)- β -methyl- Δ^2 -butene yields only an unidentified hydration product, and α -di(benzylsulphonyl)- Δ^2 -butene is unchanged under these conditions. J. D. R.

3:4-Diphenylthiophen sulphone and its hydrogenation. H. J. BACKER, C. C. BOLT, and W. STEVENS (Rec. trav. chim., 1937, **56**, 1063—1068).—3:4-Diphenylthiophen in $CHCl_3$ with BzO_2H yields 3:4-diphenyl- Δ^2 -thiacyclopentadiene 1:1-dioxide (I), m.p. 171° (decomp.), reduced (Zn-AcOH) to 3:4-diphenyl- Δ^3 -thiacyclopentene 1:1-dioxide (II), m.p. 183—184°, which is the compound described by Hinsberg (A., 1916, i, 66) as (I). Hydrogenation (Pt- H_2 in AcOH) of (I) yields successively (II), 3:4-diphenylthiacyclopentane 1:1-dioxide, m.p. 183—184°, and 3:4-dicyclohexylthiacyclopentane 1:1-dioxide, m.p. 143—145°. J. D. R.

Sulphone of 1:3-ditert.-butylbutadiene. H. J. BACKER and J. STRATING (Rec. trav. chim., 1937, **56**, 1069—1092).— γ -Hydroxy- ϵ -keto- $\beta\beta\gamma\zeta$ -pentamethylheptane is reduced (Na -EtOH- C_6H_6) to $\beta\beta\gamma\zeta$ -pentamethylheptane- $\gamma\epsilon$ -diol, b.p. 120—123°/12 mm., m.p. 90—91°, which at 100° with I yields $\alpha\gamma$ -ditert.-butylbutadiene (I). This with SO_2 in Et_2O yields 2:4-ditert.-butyl- Δ^3 -thiacyclopentene 1:1-dioxide (II), m.p. 70°, hydrogenated (Pd- H_2) to 2:4-ditert.-butylthiacyclopentane 1:1-dioxide, m.p. 76—76.5°. With O_3 in H_2O (I) yields H_2CO_2 . Oxidation of (II) ($KMnO_4$ - Na_2CO_3 in aq. $COMe_3$) yields 3:4-dihydroxy-2:4-ditert.-butylthiacyclopentane 1:1-dioxide (III), m.p. 192.5° (diacetate, m.p. 144—144.5°), and an alcohol, $C_{12}H_{22}O_4S$, m.p. 157.5° (acetate, m.p. 101°). Ozonisation of (II) in AcOH, $CHCl_3$, or aq. $CHCl_3$ yields a peroxide (IV), m.p. 127.5—128.5° (probably pinacolylsulphonyltert.-butylmethaneisocarboxylic acid), which is isomerised by heat or by $NaOMe$ to pinacolylsulphonyltert.-butylacetic acid (V), m.p. 145—146° (*Na* salt; *Na_2* derivative; *Me* ester, m.p. 115—116°), which with O_3 yields Bu^vCO_2H ,

and with Ac_2O yields a compound, $C_{12}H_{20}O_4S$, m.p. 106°, probably $CHBu^v \begin{smallmatrix} CO-O \\ SO_2-CH \end{smallmatrix} CBu^v$. With CH_2N_2 , (V) yields a dimethyl derivative, m.p. 78—79°, which with aq. KOH regenerates (V). Reduction of (IV) (H_2 -Pt) yields a trioxide, $C_{12}H_{22}O_3S$, m.p. 126.5—127°, of unknown structure, and 4-hydroxy-3-keto-2:4-ditert.-butylthiacyclopentane 1:1-dioxide (VI), m.p. 82—83°, also formed from (III) by oxidation [$Pb(OAc)_4$ in C_6H_6] [acetate, m.p. 106—106.5°; chloride, by PCl_5 on (VI) in $CHCl_3$, m.p. 156°]. When treated with Na in EtOH, (VI) yields pinacolylsulphonyl- $\beta\beta$ -dimethylpropane, m.p. 79.5°, which with CH_2N_2 affords a *Me* derivative, m.p. 30—32°. With PCl_5 in $CHCl_3$ (III) gives impure 3:4-dichloro-2:4-ditert.-butylthiacyclopentane 1:1-dioxide, m.p. 114—115°, which with KOH-EtOH yields 2:4-ditert.-butylthiacyclopentane 1:1-dioxide, m.p. 53—53.5°. $CH_2Br \cdot COBu^v$ and Na_2S in EtOH yield dipinacolyl sulphide, m.p. 53.5—54° (monoxime, m.p. 109—109.5°; dioxime, m.p. 162.5—163°), oxidised (BzO_2H in $CHCl_3$) to dipinacolyl sulphone (VII), m.p. 101°. This with Br in CCl_4 gives $\alpha\alpha'$ -dibromodipinacolylsulphone, m.p. 119—120°, which when hydrolysed (KOH) or reduced (Zn-AcOH) regenerates (VII). With Na in MeOH (VII) yields a Na_2 salt, which when treated with MeI in C_6H_6 gives $\alpha\alpha'$ -dimethyldipinacolylsulphone (VIII), m.p. 208°, the structure of which is confirmed by the following synthesis; $CHMeBr \cdot COBu^v$ and Na_2S in EtOH yield dimethyldipinacolylsulphone (an oil), oxidised (BzO_2H) to (VIII). With Na (1 atom) and MeI (1 mol.), (VII) yields α -methyldipinacolylsulphone, m.p. 77—78°, whilst with $Al-Hg$ in EtOH, 3:4-dihydroxy-3:4-ditert.-butylthiacyclopentane 1:1-dioxide, m.p. 107° (diacetate, m.p. 112.5—113°), is formed. J. D. R.

Synthesis of 1-methyl-2-sec.-butylpyrrolidine. G. P. MENSCHIKOV (J. Gen. Chem. Russ., 1937, **7**, 1632—1634).— $OMe \cdot [CH_2]_3 \cdot I$ in Et_2O , Mg , and $CHMeEt \cdot CN$ yield η -methoxy- γ -methylheptan-8-one, b.p. 187—188.5°, the oxime, b.p. 147°/24 mm., of which is reduced by Na in iso - $C_5H_{11} \cdot OH$ to yield 8-amino- η -methoxy- γ -methylheptane, b.p. 205—205.5°. This, heated with HBr at 150—155° for 12 hr., gives 2-sec.-butylpyrrolidine, b.p. 164.5—165.5° [*1-Me* derivative (I), b.p. 163—163.5° (picrate, m.p. 126—127°)]. (I) is not identical with *dl*-dihydrode-*N*-methylheliotridane. R. T.

Pyrrole derivatives. I. J. RINKES (Rec. trav. chim., 1937, **56**, 1142—1152).—4-Nitro-2-acetylpyrrole is nitrated to 4:5-dinitro-2-acetylpyrrole (I), m.p. 114° (cf. Ciamician *et al.*, A., 1886, 718), and 2:4-dinitropyrrole. 5-Nitro-2-acetylpyrrole on nitration gives 3:5-dinitro-2-acetylpyrrole, m.p. 151°, and (I). *Me* 5-nitropyrrole-2-carboxylate is nitrated to *Me* 3:5-dinitropyrrole-2-carboxylate, m.p. 118—119°, hydrolysed (H_2SO_4) to the 2-carboxylic acid, m.p. 161°, which with quinoline at 170° gives 2:4-dinitropyrrole. *Me* pyrrole-2-carboxylate with I in $NaOH$ -aq. KI yields *Me* 3:4:5-tri-iodopyrrole-2-carboxylate, m.p. 232°, hydrolysed by aq. KOH to tetraiodopyrrole and 3:4:5-tri-iodopyrrolecarboxylic acid, decomp. 180—190°, which is nitrated (HNO_3 - Et_2O - Ac_2O) to

3:4:5-tri-iodo-2-nitropyrrole. An improved prep. of Me₂ pyrrole-2:5-dicarboxylate is described.

J. D. R.

Dihydroxy[di]pyrroletripalladium penta-hydrochloride. P. SACCARDI and L. DELAVIGNE (*Gazzetta*, 1937, 67, 611—613).—PdCl₂ and pyrrole in H₂O give a black substance, C₈H₉O₂N₂Cl₅Pd₃.

E. W. W.

Lines attributed to a possible pyrrolenine form in the Raman spectrum of pyrrole.—See A., 1937, I, 599.

Raman spectrum of N-deuteropyrrole.—See A., 1937, I, 599.

Piperidino-derivatives.—See B., 1937, 1315.

Halogen derivatives of 2:4-diketo-3:3-di-alkyl-1:2:3:4-tetrahydropyridines.—See B., 1937, 1316.

Nitrogen compounds from petroleum distillates. X. Purification of nitrogen bases with zinc chloride. R. I. MAHAN and J. R. BAILEY (*J. Amer. Chem. Soc.*, 1937, 59, 2449—2450; cf. B., 1937, 204).—C₅H₅N or crude bases from, e.g., petroleum are freed from H₂O, hydrocarbons, phenols, and S compounds by heating (1 hr.) at 80° with ZnCl₂ to form B₂ZnCl₂, and then removing all constituents volatile at <320°. At >320° the double salt decomposes to give the purified base. Crude hydrochlorides are similarly treated with addition of a slight excess of NaOH to avoid formation of (B,HCl)₂ZnCl₂.

R. S. C.

Action of acid chlorides on 2-nitroaminopyridine. M. I. KABATSHNIK (*J. Gen. Chem. Russ.*, 1937, 7, 1749—1753).—2-Nitroaminopyridine and BzCl or p-NO₂-C₆H₄-COCl at 40° (12 hr.) yield 5-chloro-2-benzoyloxy-, m.p. 95—95.5°, or 2-p-nitrobenzoyloxy-pyridine, m.p. 142—143°.

R. T.

Quinolpyridinium and quinol-α-picolinium salts. E. BUCHTA (*Ber.*, 1937, 70, [B], 2339—2343).—The salts with org. acids are produced readily and in very good yield by the dropwise addition of molar proportions of C₅H₅N and acid to p-benzoquinone in CHCl₃ at 15—20°. The following quinolpyridinium salts [cf. (I)] are described: formate (I) (R = ·O-CHO), decomp. 174—175°; acetate, m.p. 206° (decomp.); benzoate, m.p. 173°, also +0.5EtOH. (I) is converted by conc. HCl into the corresponding chloride and by 70% HClO₄ into the perchlorate, m.p. 238—239°; it is also obtained from quinolpyridinium betaine. 2-Methylpyridine gives quinol-2-methylpyridinium formate, decomp. 202—204°, transformed into the chloride, m.p. 248—250° after softening.

H. W.

Mixed polymerisation. O. SCHMITZ-DUMONT, H. DIEBOLD, and K. THÖMKE (*Ber.*, 1937, 70, [B], 2189—2199).—"Mixed polymerisation" is defined as the union of two dissimilar ethylenic mols. to a compound similar to that derived from CH₂:CPh₂. Treatment of skatole (I) with CH₂:CPh₂ in AcOH-H₂SO₄ gives α- (II), m.p. 173°, and β- (III) 3-methylindolebisdiethylene, C₃₃H₃₇N, m.p. 291°. (II) contains one active H (Zerevitinov); it does not react

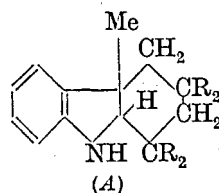
with NaOAc and boiling Ac₂O or with keten in COMe₂. With Br in AcOH (II) yields HBr and a product, C₃₇H₃₂NBr, m.p. 203.5—204.5°, transformed by NaNO₂ in AcOH into the substance, C₃₇H₃₁O₄N₂Br, m.p. 192° (decomp.). Treatment of (II) with NaNO₂ in AcOH affords a C-NO₂-compound, C₃₇H₃₂O₂N₂, m.p. 255°, reduced by Zn and AcOH to the NH₂-compound, m.p. 192—193° (which gives two Ac derivatives, m.p. 235—236° and m.p. 265—266°, respectively), and an isomeric N-NO₂-compound, m.p. 184°, reduced by Zn dust and AcOH to (II). With fuming HNO₃ in AcOH (II) gives a (NO₂)₂-compound, C₃₇H₂₉O₄N₃, m.p. 193—194°. CrO₃ in AcOH at 25° converts (II) into a ketone, C₃₆H₃₁O₂N, m.p. 168—170° (oxime, m.p. 189—190°), which does not react with HNO₂ but when treated with molten KOH gives the monocarboxylic acid, C₂₃H₁₉O₂N, m.p. 291—294° when slowly heated (also +EtOH), which with NaNO₂ in AcOH affords a substance, m.p. 208—210° (decomp.). Br in CHCl₃ and (III) give HBr and a mixture of products, from which the compound C₃₇H₃₂NBr, m.p. 226—228°, is isolated. Di-p-tolylethylene and (I) yield only 3-methylindolebisdi-p-tolylethylene, m.p. 192—194°, analogous to (II). This is transformed by AcOH-NaNO₂ into the C-NO₂-compound, C₄₁H₄₀O₂N₂, m.p. 230.5—231.5° (decomp.), and the N-NO₂-derivative, m.p. 182—183° (decomp.), reduced to the original material. Dianisylethylene and (I) similarly afford 3-methylindolebisdianisylethylene, m.p. 237.5—238°. The skatolebisdiaryethylenes have probably the structure A. CPhMe:CH₂ and (I) afford 3-methylindoletri-α-methylstyrene, m.p. 154—155° (apparently accompanied by pentameric α-methylstyrene, m.p. 114—116°); it gives a N-NO₂-compound, C₃₆H₃₈O₂N₂, m.p. 134—135°, with small amounts of the C-NO₂-derivative.

H. W.

Quinoline compounds as sources of medicinal compounds. V. Anæsthetics of the 8-amino-6-alkoxyquinoline series. O. J. MAGIDSON and A. L. MIDSHOJAN (*J. Gen. Chem. Russ.*, 1937, 7, 1557—1563).—NEt₂·CH₂:CMe₂·CH₂Br (I) is condensed with a series of 8-amino-6-alkoxyquinoline derivatives, to yield the following new (?) compounds: 8-(γ-diethylamino-ββ-dimethyl)propylamino-6-ethoxy-, b.p. 193—198°/1 mm. [dihydrochloride, m.p. 205—207° (decomp.)], -6-propoxy-, b.p. 197—204°/1.5 mm. [dihydrochloride, m.p. 214—217° (decomp.)], -6-butoxy-, b.p. 206—212°/2 mm. [dihydrochloride, m.p. 218—220° (decomp.)], and -6-benzoyloxy-quinoline, m.p. 195—198° [prepared from 8-nitro-, m.p. 104°, via 8-amino-6-benzoyloxyquinoline, m.p. 69—70° (hydrochloride, m.p. 226—228°)]. Attempted condensation of (I) with 8-amino-6-octoxyquinoline was unsuccessful.

R. T.

Constitution of quinophthalone. A. E. PORAI-KOSCHITZ, B. A. PORAI-KOSCHITZ, and S. A. LUICK (*Compt. rend. Acad. Sci. U.R.S.S.*, 1937, 16, 451—452).—2-Aminoquinoline and o-C₆H₄(CO)₂O in PhCl yield 2-quinolylphthalamic acid, m.p. 187—188°, which when fused or heated in boiling NPhMe₂ gives



N-2-quinolylphthalimide, m.p. 238—239°. Similarly, from 2-aminopyridine, N-2-pyridylphthalimide (II), m.p. 228°, is formed. The fact that (I) and (II) have no possible tautomeric modifications and are colourless is advanced as an argument for the existence of tautomeric forms in quinophthalone as suggested by Kuhn and Bär (A., 1935, 758). J. D. R.

Action of diazomethane on allyl bromide and chloride. G. CARONNA (Gazzetta, 1937, 67, 614—620).— $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Br}$ and CH_2N_2 in Et_2O give a H_2O -sol. hydrobromide, m.p. 135° (decomp.), probably of 5-methylene- Δ^2 -pyrazoline [platinichloride (I)]. The intermediate 5-bromomethylpyrazoline is isolated as the hydrobromide, m.p. 140° (decomp.). From $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Cl}$, (I) and 5-chloromethyl- Δ^2 -pyrazoline (?) [picrate, m.p. 130° (decomp.); hydrochloride; oxalate] were obtained. E. W. W.

Compounds of cadmium iodide with heterocyclic bases containing nitrogen. I. Pyramidone. P. DUQUÉNOIS (J. Pharm. Chim., 1937, [viii], 26, 353—360).—Pyramidone (I) in H_2O with Marmé's reagent or CdI_2 affords a compound (II), $\text{C}_{13}\text{H}_{17}\text{ON}_3\text{CdI}_2$, m.p. 225° (decomp.), which with aq. AgNO_3 affords AgI , (I), and $\text{Cd}\cdot\text{Cd}(\text{NO}_3)_2\cdot\text{KI}$ and (I) give (II). J. L. D.

Iminazoles. V. Derivatives of glyoxaline-4(5)-carboxylic acid. R. WEIDENHAGEN and H. WEGNER (Ber., 1937, 70, [B], 2309—2318).—4(5)-Hydroxymethylglyoxaline, readily obtained from fructose and CH_2O (A., 1937, II, 211), is oxidised by HNO_3 to the carboxylic acid (I), the Me ester of which is transformed by NH_2Me in MeOH at 160° into glyoxaline-4(5)-carboxy-methylamide, m.p. 145° after slight softening (also $+1\text{H}_2\text{O}$) (picrate, m.p. 196°). The corresponding -ethylamide, m.p. 161—162° (picrate, m.p. 193—194°), -propylamide, m.p. 121—122° (picrate, m.p. 150°), and -allylamide, m.p. 130° (picrate, m.p. 171—172°), are described. Attempts to obtain dialkylamides similarly were unsuccessful, the products being unchanged ester, (I), or glyoxaline. SOCl_2 has no action on (I), which reacts readily with PCl_5 which has acquired a trace of moisture but not with fresh PCl_5 , giving the corresponding chloride, which reacts smoothly with primary or sec. amines. Glyoxaline-4(5)-carboxydimethylamide has b.p. 165—170°/0.4 mm., m.p. 90—91° [oxalate, $\text{C}_7\text{H}_{10}\text{O}_3\text{N}_3$, m.p. 204° (decomp.); picrate, m.p. 200—202°; very hygroscopic hydrochloride]. The corresponding diethylamide, b.p. 168—175°/0.4 mm. [oxalate, m.p. 166° (slight decomp.); picrate, m.p. 158—159°; very hygroscopic hydrochloride], and dipropylamide, b.p. 180—190°/0.4—0.5 mm., m.p. 69—70° (oxalate, m.p. 160—161°; picrate, m.p. 147—148°; also $+1\text{H}_2\text{O}$; very hygroscopic hydrochloride), are described. H. W.

Degradation of histidine by ascorbic acid and thiolacetic acid. P. HOLTZ (Z. physiol. Chem., 1937, 250, 87—103).—Discrepancies between the author's results and those of Abderhalden (A., 1937, II, 371) and Edlbacher and von Segesser (*ibid.*, 433) are explained, the conclusions of these workers being criticised. The intermediate product of the degradation is not identical with that of the action of

histidase. Fe catalyses the action of ascorbic acid (I) and thiolacetic acid (II) but the deamination caused by Cu is not affected by the addition of (I) or (II). W. McC.

Derivatives of piperazine. XII. α -Amino-ketones derived from N-phenylpiperazine and derivatives. B. L. HAMPTON and C. B. POLLARD (J. Amer. Chem. Soc., 1937, 59, 2446—2447; cf. A., 1937, II, 520).—N-Phenylpiperazine (2 mols.) and the appropriate phenacyl halide (1 mol.) in Et_2O or 1 mol. of each with a slight excess of Na_2CO_3 in hot EtOH give N-phenacyl-, m.p. 106—108° (210—212°; 157—158°), N-p-methyl-, m.p. 136—138° (235—237°; 184—185°), N-p-methoxy-, m.p. 145—147° (227—229°; 182—183°), and N-p-chloro-phenacyl-N'-phenylpiperazine, m.p. 131—133° (225—227°; 169—170°). M.p. in parentheses are those of the hydrochlorides and oximes, respectively. M.p. are corr. R. S. C.

Tetra-alkylbarbituric acids. M. T. BUSH and T. C. BUTLER (J. Pharm. Exp. Ther., 1937, 61, 139—147).—1:3:5:5-Tetramethyl-, m.p. 109—110°, and 5:5-dimethyl-1:3-diethyl-barbituric acid, b.p. 93—96°/2 mm., are obtained from CH_2N_2 or CHMeN_2 and 5:5-dimethylbarbituric acid. The following barbituric acids are formed by the action of Me_2SO_4 or Et_2SO_4 and NaOH on the appropriate 5:5-disubstituted barbituric acid: 1:3-dimethyl-5:5-diethyl-, m.p. 36—38°, b.p. 92—94°/2 mm.; 1:3-dimethyl-5-ethyl-5-isopropyl-, b.p. 98—99°/2 mm.; 1:3-dimethyl-5-ethyl-5-n-butyl-, b.p. 108—110°/2 mm.; 1:3-dimethyl-5-ethyl-5-(α -methylbutyl)-, b.p. 116—118°/2 mm.; 1:3-dimethyl-5:5-diallyl-, m.p. 53—54° (uncorr.), and 1:3:5:5-tetraethyl-, b.p. 110—112°/8.5 mm. The alkylated barbituric acids produce marked narcotic and convulsant effects on rabbits and mice, the exact nature of the action varying with compound and animal. W. O. K.

5-Triphenylmethylbarbituric acid. H. W. COLES (J. Amer. Chem. Soc., 1937, 59, 2468—2469).—Contrary to Berggårdh (Acta Acad. Abo. Math. Phys., 1935, 9, No. 3), triphenylmethylmalonic acid (prep. by the Mg-malonic derivative in 80% yield), m.p. 131—132°, $\text{CO}(\text{NH}_2)_2$, and NaOEt give in 4 hr. 16.8% of 5-triphenylmethylbarbituric acid, m.p. 197.6° (corr.), pharmacologically inactive, which with NaOH gives $\text{CPh}_3\cdot\text{OH}$, acetyltriphenylmethylcarbamide, m.p. 141°, and another substance. Longer heating leads to decomp. R. S. C.

Pyrimidines. CLVII. Action of chlorine on 2:4-diketotetrahydropyrimidines. T. B. JOHNSON and J. M. SPRAGUE (J. Amer. Chem. Soc., 1937, 59, 2436—2439).—Interaction of uracil or 5-chlorouracil with Cl_2 in an alcohol involves chlorination of C_5 and addition of ROH , leading to 5:5-dichloro-2:4-diketo-6-methoxy-, m.p. 225—226°, -ethoxy-, m.p. 234—235°, - β -chloroethoxy-, m.p. 195—196°, and -n-butoxy-hexahydropyrimidine, m.p. 172—173°. Thymine gives similarly 5-chloro-2:4-diketo-6-methoxy-, m.p. 221—222°, - β -chloroethoxy-, m.p. 200—201°, -ethoxy-, m.p. 223—224°, and -n-butoxy-5-methyl-tetrahydropyrimidine, m.p. 193—194°, 5-chloro-5-bromo-, m.p. 216—217°, and -nitro-2:4-diketo-6-methoxytetrahydropyrimidine, m.p. 216—217° (de-

comp.), are similarly obtained. The ethers are interconvertible by HCl-ROH and are obtained from the 5-chloro-6-hydroxy-compound by HCl-ROH or from the 5:6- Cl_2 -compound by ROH . Reduction of the ethers by Sn-HCl gives the 5-substituted diketotetrahydropyrimidine. EtOCl in CHCl_3 at 0° adds to thymine or 5-chlorouracil. Cl_2 in CHCl_3 gives 5:6-dichloro-2:4-diketo-5-methyl-, solid, and 5:5:6-trichloro-2:4-diketo-hexahydropyrimidine (I), m.p. 200—260° (decomp.). 5:5-Dichloro-2:4-diketo-6-acetoxy-hexahydropyrimidine, m.p. 174—175°, is obtained from uracil or 5:5-dichloro-6-hydroxy-2:4-diketo-6-methoxyhexahydropyrimidine by Cl_2 in Ac_2O or from 5:5-dichloro-2:4-diketo-6-methoxyhexahydropyrimidine (II), m.p. 225—226°, by $\text{Ac}_2\text{O-AcOH}$, and with HCl-MeOH gives (II). With ROH (I) gives (II), 5:5-dichloro-2:4-diketo-6-ethoxy-, m.p. 234—235°, β -chloroethoxy-, m.p. 195—196°, and *n*-butoxy-hexahydropyrimidine, m.p. 172—173°. 5:5-Dichloro-2:4-diketo-6-methoxy-6-methylhexahydropyrimidine has m.p. 265—270° (decomp.). R. S. C.

Ferrottrisdi-pyridyl complex. C. FERRARI (Gazzetta, 1937, 67, 604—608; cf. A., 1935, 179).— Aq. FeSO_4 and 2:2'-dipyridyl yield an intensely red product, which with HCl and BaClO_4 yields the compound, $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2$. On adding FeSO_4 to aq. $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{SO}_4$, the extinction coeff. reaches a max. at the formation of the complex $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]$. The complexes $\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3(\text{CNS})_2$ and $\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{CNS})_2$ are also prepared; the last (magnetic susceptibility measured) probably has the structure $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]_2[\text{Fe}(\text{CNS})_6]$. E. W. W.

Optical activity without an asymmetric carbon atom. XXII. Spirans. D. RĂDULESCU and V. MOGA (Bull. Soc. Chim. România, 1936, 18, 167—175).— Et_2 di-*p*(or *o*)-nitrobenzylmalonate in $\text{HNO}_3\text{-H}_2\text{SO}_4$ at 0° affords Et_2 di-2:4-dinitrobenzylmalonate, reduced (Thiele and Dimroth's reagent) to bisaminodihydrocarbostyrylspiran (sulfate), which is resolved with *d*-tartaric acid into the *d*- and *l*-forms, $[\alpha]_D +$ and -108.6° (*d*- and *l*-hydrochlorides, $[\alpha]_D +$ and -138.7°) (cf. A., 1922, i, 1240). Part of the existing literature is reviewed. The diamine is diazotised with difficulty; the diazonium compound gives an unstable diphenol. J. L. D.

Chemiluminescent organic compounds. V. Methyl derivatives of 5-nitro- and 5-amino-phthalaz-1:4-dione. Structural features in relation to chemiluminescence. H. D. K. DREW and R. F. GARWOOD (J.C.S., 1937, 1841—1846).—The orientation of Me in the α - and β -forms of 5-amino-*N*-methylphthalaz-1:4-dione (cf. Drew *et al.*, A., 1937, II, 118) has been determined by treating the azo-compounds derived from $\beta\text{-C}_{10}\text{H}_7\text{-OH}$ with CuCl and NH_3 . 2-Methylphthalaz-1:4-dione-5-azo- β -naphthol, m.p. 334° (decomp.) (from α -form), gives an aminocupric salt and a pyridinocupric salt ($+\text{H}_2\text{O}$), whilst the 3-Me compound, m.p. 326° (decomp.) (from β -form), affords an $\text{NH}_4^+ \text{Cu}^{\text{II}}$ salt, converted by more CuCl into the Cu^{II} salt ($+\text{H}_2\text{O}$), and a pyridinocupric salt; the 2:3-Me₂ compound yields a Cu^{II} salt. Seven out of the eight possible Me derivatives have been prepared and further methylation gives the structure of the Me₂ derivatives. It is

concluded that chemiluminescence is dependent on the ion derived from the dilactim form of the cyclohydrazide. This probably forms a peroxide, directly responsible for the reaction which initiates the radiation.

3-Acetcarbamidophthalic anhydride and N_2H_4 give 5-acetcarbamidophthalaz-1:4-dione, m.p. 320° (decomp.), which is strongly chemiluminescent. 3-Acetamidophthalimide and N_2H_4 afford 3-acetamido-*N*-aminophthalimide, m.p. 163° (benzylidene derivative, m.p. 214°), converted with alkali into the chemiluminescent cyclohydrazide. 3-Aminophthalimide with NHPh-NH_2 yields 3-amino-*N*-anilino-phthalimide, m.p. 222°, and with NHMe-NH_2 gives after acidification α - and β -forms of 5-amino-*N*-methylphthalaz-1:4-diones. Condensation of NHMe-NH_2 with 2-carbethoxy-3- or -6-nitrobenzoic acid leads in each case to a mixture of α - and β -forms of 5-nitro-*N*-methylphthalaz-1:4-dione. Methylation (Me_2SO) of 5-nitrophthalaz-1:4-dione gives β -5-nitro-*N*-methylphthalaz-1:4-dione and its *O*-Me ether, also obtained from the Ag salt of 5-nitro-3-methylphthalaz-1:4-dione and MeI (cf. Zellner *et al.*, A., 1936, 1391). The Ag salt of α -5-nitro-*N*-methylphthalaz-1:4-dione and MeI yield 5-nitro-4-methoxy-2-methylphthalaz-1-one, m.p. 199—200°, reduced to the 5- NH_2 -compound, m.p. 136° (*Ac* derivative, m.p. 187°). 5-Amino-1-methoxy-3-methylphthalaz-4-one, m.p. 222° (*Ac* derivative, m.p. 220°), is similarly prepared. 5-Nitro-1-methoxyphthalaz-4-one, m.p. 269° (*Ac* derivative, m.p. 188—190°), prepared from the Ag salt of 5-nitrophthalaz-1:4-dione and MeI, is reduced to the 5- NH_2 -compound, m.p. 234°. 1:4-Dimethoxyphthalazine, m.p. 121°, is obtained by methylation of 1-methoxyphthalaz-4-one. 5-Nitro-1:4-dimethoxyphthalazine, m.p. 212—214°, is reduced to the 5- NH_2 -compound, m.p. 172—174°. 3-Acetamidophthalic anhydride and NHMe-NH_2 give α - and β -forms of 5-acetamido-*N*-methylphthalaz-1:4-diones (pure α -form, m.p. 291°). 3-Nitrophthalimide and N_2H_4 afford 3-nitro-*N*-aminophthalimide, m.p. 192° (converted into cyclohydrazide), which with 3-nitrophthalic anhydride yields 3:3'-dinitro-*N*-phthalimidophthalimide, m.p. 321°.

F. R. S.

Flazine, $\text{C}_{18}\text{H}_{16}\text{O}_5\text{N}_2$, m.p. 218—220° (hydrochloride, $+\text{H}_2\text{O}$, m.p. 140°), from saké.—See A., III, 74.

Reactions between carbylamines and pyrazolone derivatives. G. LOSCO (Gazzetta, 1937, 67, 553—557).—1-Phenyl-3-methyl-5-pyrazolone (I) (cf. A., 1937, II, 433) and *p*-NPh.N·C₆H₄.NC in C₆H₆ at the b.p. for 5 hr. give the *p*-benzeneazobenzil, m.p. 203—204°, of 1-phenyl-3-methyl-5-pyrazolone-4-aldehyde (II), from which, and *p*-NH₂·C₆H₄·N₂Ph, it is also obtained. 1:3-Diphenyl-5-pyrazolone and PhNC yield 1:3:1':3'-tetraphenyl-4:4'-methenylbispyrazolone (A., 1906, i, 544). Similarly 3-methylpyrazolone gives 3:3'-dimethyl-4:4'-methenylbispyrazolone, also obtained from 5-keto-3-methyl-4:5-dihydropyrazole-1-carboxylamide and PhNC. The assumption that these are formed by way of the anils is supported by the formation of 1:1'-diphenyl-3:3'-dimethyl-4:4'-methenylbispyrazolone from (I) and the anil of (II) (A., 1937, II, 433) in boiling C₆H₆. E. W. W.

Mol. wt. of pyrrole-blue. W. STEINKOPF and H. WILHELM (Ber., 1937, 70, [B], 2233—2234).—Condensation of pyrrole with Et isatin-1-acetate gives *Et pyrrole-blue-acetate*, m.p. $>350^\circ$, which, according to determinations of mol. wt. in C_5H_5N , $PhOH$, $C_6H_2Br_2OH$, $BzOH$, and phenanthrene, is $C_{32}H_{28}O_6N_4$. *Et cryptopyrrole-blue-acetate* is $C_{40}H_{44}O_6N_4$. The constitution assigned to pyrrole-blue by Pratesi (A., 1933, 958) cannot therefore be correct. Other proposed formulæ fail to account for its intense blue colour. H. W.

Oxazolines and thiazolines. I. Reaction of hydrothiocyanic acid with ethylene oxide. P. G. SERGEEV and B. S. KOLITSCHIEV. **II. Preparation of 2-thioloxazole.** P. G. SERGEEV and S. N. IVANOVA (J. Gen. Chem. Russ., 1937, 7, 1390—1396, 1495—1500).—I. $(CH_2)_2O$ and $HCNS$ in Et_2O at -10° yield β -thiocyanoethyl alcohol (I), b.p. $106-107^\circ/0.012$ mm., which changes at room temp. (5 days) into 2-thion-3- β -hydroxyethyltetrahydroglyoxaline, m.p. 168.5° (decomp.). In Et_2O and HCl at 0° (I) yields the hydrochloride, m.p. 121.5° , of 2-iminothioxaline, which isomerises at 80° to give a substance, m.p. 106° , not containing ionisable Cl .

III. $NH\cdot[CH_2]_2\cdot OH$ (II) in $EtOH$ and CS_2 react at $>10^\circ$ giving $OH\cdot[CH_2]_2\cdot NH\cdot CS_2H, NH_2\cdot[CH_2]_2\cdot OH$, which with $ClCO_2Me$ produces $OH\cdot[CH_2]_2\cdot NH\cdot CS\cdot S\cdot CO_2Me$, m.p. $66-67^\circ$. This in 2—3 days at room temp. or at the m.p. becomes 2-thioltetrahydro-oxazole, m.p. $96-97^\circ$, also obtained from (II) and $CSCl_2$. R. T.

Aminophenyl-2-oxazolines as local anæsthetics. M. T. LEFFLER and R. ADAMS (J. Amer. Chem. Soc., 1937, 59, 2252—2258).—Aminophenyl-2-oxazoline hydrochlorides are local anæsthetics, but are too acidic for use; the 5-dialkylaminoalkyl derivatives are too toxic. The following are described: $p\text{-}CH_2Cl\cdot C_6H_4\cdot COCl$, b.p. $126-128^\circ/6$ mm.; $OH\cdot CHMe\cdot NH_2$ (from propylene oxide, aq. NH_3 , and a trace of $NaOH$ at 0°); p -amino- β -phenylethyl alcohol (from $NH_2\cdot CHPh\cdot CO_2Et$), b.p. $125-127^\circ/3$ mm. (hydrochloride, m.p. $146-147^\circ$; Bz derivative, m.p. $149-150^\circ$); β -aminohexanol (hydrochloride, m.p. $93-94.5^\circ$); γ -aminobutan- β -ol, b.p. $160-162^\circ$ (corr.)/742 mm.; $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot NH_2\cdot HCl$, m.p. $104.5-105.5^\circ$; $CH_2Br\cdot CH_2\cdot NH_2\cdot HBr$ (from $OH\cdot[CH_2]_2\cdot NH_2$ and PBr_3); $CHMeBr\cdot CH_2\cdot NH_2\cdot HBr$, m.p. $157-159^\circ$; α -chloro- β -aminohexane hydrochloride, m.p. $116.5-118^\circ$. The acid chloride with the aminoalkyl halide or alcohol, or $p\text{-}NO_2\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$ with the *sec.* base, gives *o*-, m.p. $112.5-123.5^\circ$, *m*-, and *p*-nitro-, m.p. $121-122^\circ$, 3-nitro-4-methoxy-, m.p. $110-111^\circ$, and *p*-chloromethyl-benz- β -bromoethylamide, m.p. $117-118^\circ$, *o*-, *m*-, and $p\text{-}NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CHMeBr$, m.p. $129-129.5^\circ$, and *p*-nitrobenz- β -hydroxyisobutylamide, m.p. $134.5-135.5^\circ$, *p*-nitrobenz- β -hydroxy- α -methylpropylamide, unstable, *p*-nitrobenz- α -chloromethyl-*n*-amylamide, m.p. $116.5-118^\circ$, β -chloro- α -phenylethylamide, m.p. $132.5-133.5^\circ$, γ -chloro- β -hydroxypropylamide, m.p. $110-111^\circ$, γ -diethyl-hmino- β -hydroxypropylamide (hydrochloride, m.p. $163-164.5^\circ$), γ -dibutylamino- β -hydroxypropylamide, m.p. $83.5-84.5^\circ$, 2-chlorocyclohexylamide, m.p. $156-$

157° , and 2-hydroxycyclohexylamide, m.p. $210.5-211.5^\circ$, and *m*-nitrocinnam- β -bromoethylamide, m.p. $107-108^\circ$. Ring-closure by $NaOH$ in aq. $EtOH$ at $70-75^\circ$, in H_2SO_4 at $55-60^\circ$, or by $SOCl_2$ gives 2-nitro-, reduced by Fe to the corresponding aminophenylloxazolines, of which the following are described (m.p. being those of the NO_2 - and NH_2 -compounds successively, m.p. in parentheses being those of the hydrochlorides of the NH_2 -compounds): 2-*o*-, m.p. $52-53^\circ$, 55-56°, *m*-, m.p. $118-119^\circ$, 125-126° (also obtained by H_2 - PtO_2 in 95% $EtOH$ containing a trace of $AcOH$ at 2—3 atm.), and *p*-nitrophenyl-, m.p. $178-178.5^\circ$, 160—161° [also prepared by hydrogenation; hydrochloride, m.p. $254-255^\circ$ (decomp.)], 2-3'-nitro-4'-methoxyphenyl-, m.p. $122-123^\circ$, 126-5—127.5°, 2-*p*-chloromethylphenyl-, m.p. $70-71^\circ$, 2-*o*-, an oil (hydrochloride, m.p. $119-120^\circ$), m.p. $41.5-42^\circ$, 2-*m*-, m.p. $86-87^\circ$, 115-116°, and *p*-nitrophenyl-5-methyl-, m.p. $134-135^\circ$, 128.5-129.5° (213-214°), 2-*m*-, m.p. $81-82^\circ$, 122-123°, and *p*-nitrophenyl-5:5-dimethyl-, m.p. $143-144^\circ$, 145-146°, 2-*p*-nitrophenyl-4:5-dimethyl-, m.p. $122.5-123.5^\circ$, 211-212°, 4-phenyl-2-*p*-nitrophenyl-, m.p. $108.5-109^\circ$, 150-150.5° [239-240° (decomp.)], 2-*p*-nitrophenyl-4-*n*-butyl-, m.p. $46-47^\circ$, an oil (197-197.5°), 5-chloromethyl-, m.p. $117-118^\circ$, —, 5-diethylaminomethyl-, m.p. $57-57.5^\circ$, b.p. $205-206^\circ/2.5$ mm. [190-191° (decomp.)], 5-dibutylaminomethyl-, m.p. $60.5-61^\circ$, an oil (204-205° (decomp.)), and 4:5-cyclohexano-, m.p. $129.5-130.5^\circ$ (+ H_2O , m.p. $99-100^\circ$), 155-156°, 2-*m*-nitrostyryl-, m.p. $117-118^\circ$, 144-145°, 2-*p*-diethylaminophenyl-, —, b.p. $152-154^\circ/2$ mm. (150.5-151°), and 2-3':5'-dibromo-4'-aminophenyl-, —, m.p. $193-194^\circ$. R. S. C.

2-Aminophenylpentoxazolines. A. NOVELLI and R. ADAMS (J. Amer. Chem. Soc., 1937, 59, 2259—2260).— $Br\cdot[CH_2]_3\cdot NH_2\cdot HBr$ [prep. from $Br\cdot[CH_2]_3\cdot N(CO_2C_6H_4\cdot o)$ and $NO_2\cdot C_6H_4\cdot COCl$ in C_6H_6 -aq. $NaOH$ give *p*-, m.p. $108.5-109.5^\circ$, *m*-, and *o*-nitrobenz- γ -bromopropylamide, m.p. $118-119^\circ$, converted by KOH - $EtOH$ at $60-65^\circ$ into 2-*o*-, m.p. 145° , *m*-, and *p*-nitrophenylpentoxazoline, m.p. $118-119^\circ$. The derived (Fe) NH_2 -compounds, m.p. $170-171^\circ$ (dihydrochloride, m.p. $192-193^\circ$), 139-139.5° (dihydrochloride, m.p. $154-155^\circ$), and b.p. $137^\circ/4$ mm. (dihydrochloride, m.p. $128-131^\circ$), respectively, are local anæsthetics, but hydrolyse too readily and are too toxic for use. Benz-, m.p. $151-152^\circ$, and *p*-nitrobenz-2-bromocyclohexylamide, m.p. $160-161^\circ$, do not yield pentoxazolines. R. S. C.

Aminophenyl-thiazolines and -thiazines. S. H. BABCOCK and R. ADAMS (J. Amer. Chem. Soc., 1937, 59, 2260—2261).—*p*-Nitrobenz- β -chloroisobutylamide, m.p. $131-132^\circ$ (all m.p. except this are corr.) (from $CMe_2Cl\cdot CH_2\cdot NH_2$ and $p\text{-}NO_2\cdot C_6H_4\cdot COCl$), and P_2S_5 at $100-110^\circ$ give 2-*p*-nitrophenyl-5:5-dimethylthiazoline, m.p. $117-118^\circ$, reduced (Fe powder, very dil. HCl) to the NH_2 -derivative, m.p. $141-142^\circ$. 2-*p*-Nitrophenyl-thiazoline, m.p. $156-157^\circ$, 5-methylthiazoline, m.p. $108-108.5^\circ$, and 5:6-dihydro-1:3:4-thiazine, m.p. $137-139^\circ$, similarly prepared from *p*-nitrobenz- β -bromoethyl-, β -bromopropyl-, and γ -bromopropyl-amide, respectively, are reduced to the NH_2 -derivatives, m.p. $163-164^\circ$, $105-106^\circ$, and

115—115.5°, respectively. 2-*m*-Nitrophenyl-thiazoline, m.p. 131—132°, 5-methylthiazoline, m.p. 70.5—71.5°, and 5:6-dihydro-1:3:4-thiazine, m.p. 90—91°, are obtained by nitration of the respective 2-Ph derivatives; the corresponding NH_2 -derivatives have m.p. 66—67°, 58—59°, and 75—76°, respectively.

H. B.

Aminophenyl-oxazoles and -thiazoles. B. S. FRIEDMAN, M. SPARKS, and R. ADAMS (J. Amer. Chem. Soc., 1937, 59, 2262—2264).—Salts of 2-aminophenyl-oxazoles and -thiazoles are local anæsthetics, but are too acidic for use. 2-Phenyl-4-methyl-oxazole (from $\text{CH}_2\text{Br}\cdot\text{COMe}$ or, less well, $\text{CH}_2\text{Cl}\cdot\text{COMe}$, NH_2Bz , and CaCO_3 at 120—130°, b.p. 92—95°/5 mm. (hydrochloride, m.p. 72°; picrate, m.p. 111°), with H_2SO_4 and fuming HNO_3 at <0° gives the *p*- NO_2 -derivative, m.p. 146° (hydrolysed by HCl to *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$), reduced by $\text{Fe}\cdot\text{H}_2\text{O}$ to 2-*p*-aminophenyl-4-methyl-oxazole, m.p. 129°. 2-Phenyl-, m.p. 50°, b.p. 128—130°/5 mm., 2-*p*-nitrophenyl-, m.p. 211°, and 2-*p*-amino-phenyl-4:5-dimethyl-oxazole, m.p. 153°, are similarly prepared; *m*- (but not *p*-) $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, $\text{CH}_2\text{Cl}\cdot\text{COMe}$, and CaCO_3 give 5% of 2-*m*-nitrophenyl-4-methyl-oxazole, m.p. 100°, and thence the NH_2 -compound, m.p. 97°. 2-Phenyl-, b.p. 266°/743 mm., 110—115°/8 mm., and 2-phenyl-4-methyl-thiazole, b.p. 275—277°/750 mm., 111°/6 mm., are prepared. $\text{CHMeCl}\cdot\text{COMe}$ or $\text{CH}_2\text{Cl}\cdot\text{COEt}$ with $\text{PhCS}\cdot\text{NH}_2$ and NaOH in EtOH give 2-phenyl-4:5-dimethyl-, b.p. 126—128°/6 mm., and 4-ethyl-thiazole, m.p. 117—118°, respectively. *p*- $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CS}\cdot\text{NH}_2$ (from $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$, NH_3 , and H_2S in EtOH at 100°, m.p. 159—161.5°, with $\text{OEt}\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$, $\text{CH}_2\text{Cl}\cdot\text{COMe}$, $\text{CHMeCl}\cdot\text{COMe}$, or $\text{CH}_2\text{Cl}\cdot\text{COEt}$ gives 2-*p*-ethoxyphenyl-thiazole, b.p. 139—141°/6 mm., 4-methyl-, b.p. 160—161°/6 mm., 4:5-dimethyl-, m.p. 84.6—86°, and 4-ethyl-thiazole, b.p. 150—152°/6 mm., respectively. Nitration and reduction affords 2-*p*-nitro-, m.p. 147.5—148.5°, and -amino-phenyl-, m.p. 123—124°, 2-*p*-nitro-, m.p. 105.5—106.5°, and -amino-phenyl-4-methyl-, m.p. 112.5—113.5°, 2-*p*-nitro-, m.p. 169—169.5°, and -amino-phenyl-4:5-dimethyl-, m.p. 130.5—131.5°, 2-*p*-nitro-, m.p. 79.5—80°, and -amino-phenyl-4-ethyl-, m.p. 106.5—107°, 2-3'-nitro-, m.p. 107.3—108.3°, and -amino-4'-ethoxyphenyl-, m.p. 96.5—97.5°, 2-3'-nitro-, 130.5—132°, and -amino-4'-ethoxyphenyl-4-methyl-, m.p. 126—127°, 2-3'-nitro-, m.p. 140.2—141.2°, and -amino-4'-ethoxyphenyl-4:5-dimethyl-, m.p. 163.5—164.5°, 2-3'-nitro-, m.p. 71—71.5°, and -amino-4'-ethoxyphenyl-4-ethyl-thiazole, m.p. 109—109.5°.

R. S. C.

isoOxazole group. IV. Action of α -chloro-benzaldoxime on β -ketonic esters. A. QUILICO and R. FUSCO (Gazzetta, 1937, 67, 589—603).— $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ and $\text{CPhCl}\cdot\text{N}\cdot\text{OH}$ (I) in EtOH yield the *Et* ester, m.p. 48°, of 3-phenyl-5-methylisooxazole-4-carboxylic acid, m.p. 189—190° (acid chloride, m.p. 24—25°; amide, m.p. 209°; anilide, m.p. 193—193.5°). The compound described by Benary (A., 1909, i, 890) is probably the isomeric *Et* 5-phenyl-3-methylisooxazole-4-carboxylate (cf. A., 1915, i, 714 etc.). $\text{COBu}^+\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ and (I) yield the *Et* ester, m.p. 114°, of 3-phenyl-5-tert.-butylisooxazole-4-carboxylic acid, m.p. 172—173° (acid chloride), of which

the amide, m.p. 153—154°, is also obtained by action of $\text{KOH}\cdot\text{EtOH}$ on the corresponding nitrile, b.p. 175°/20 mm., obtained from (I) and $\text{COBu}^+\cdot\text{CHNa}\cdot\text{CN}$. $\text{CHNaBz}\cdot\text{CO}_2\text{Et}$ and (I) give the *Et* ester, m.p. 191°, of 3:5-diphenylisooxazole-4-carboxylic acid (A., 1922, i, 52). $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ (III) and (I) give the *Et* ester of 3-phenylisooxazole-4:5-dicarboxylic acid (IV) ($+\text{H}_2\text{O}$), m.p. 160—170° (decomp., evolving CO_2) (Na_2 and Ag_2 salts; dichloride; diamide, m.p. 225°, which decomposes before yielding an imide). The first hydrolysis product of (IV) [in the prep. of which 3-phenylisooxazole (?) is also formed] is an *Et* ester, most probably 3-phenyl-4-carbethoxyisooxazole-5-carboxylic acid, m.p. 87° (*Na*, *Ag*, and *Ba* salts; acid chloride; amide, m.p. 101—102°). In the above reactions, secondary products are also formed, e.g., 3:4-diphenyl-1:2:5-oxadiazole 5-oxide, from (I) and (III).

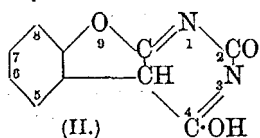
E. W. W.

Dihydronaphtho-pyrazoles and -isooxazoles.

K. VON AUWERS and A. E. NOLD (J. pr. Chem., 1937, [ii], 150, 57—67; cf. A., 1932, 863).—1-Keto-2-hydroxymethylenetetrahydronaphthalene (I) is transformed into its acetylhydrazone, m.p. 141°, which, like the benzoylhydrazone, is not transformed into an acylated pyrazole by POCl_3 . Similar treatment of the carbethoxyhydrazone gives a small yield of 2-carbethoxydihydronaphthopyrazole, m.p. 66—67°. The semicarbazone, m.p. 199—200°, of (I) is converted into dihydronaphthopyrazole, m.p. 122—122.5°. This with NaOMe and MeI yields a mixture of 1-, b.p. 174°/12 mm. (picrate, m.p. 187—187.5°), and 2-, b.p. 180°/12 mm. (picrate, m.p. 168—169°), -methyl-dihydronaphthopyrazole. Spectrochemical investigation of these compounds shows the limited applicability of rules which have proved trustworthy with simple heterocyclic substances and the restricted val. of the evidence for the establishment of constitution. It is therefore impossible by this means to decide whether the parent compound corresponds with its 1- or 2-derivatives. The product of the action of $\text{NH}_2\text{OH}\cdot\text{HCl}$ on (I) at room temp. is exclusively 4:5-dihydronaphthoisooxazole, b.p. 163°/11—12 mm. (after purification through its additive compound with HgCl_2 , m.p. 142° after softening at 132°), since it is quantitatively converted by NaOEt at low temp. into 2-cyano-1-keto-1:2:3:4-tetrahydronaphthalene, m.p. 79°.

H. W.

Condensation of benzene with alloxan. H. M. BARNES and S. M. McELVAIN (J. Amer. Chem. Soc., 1937, 59, 2348—2351; cf. A., 1935, 1132).—Alloxan monohydrate, C_6H_6 , and 20% oleum at 75—80° give 35—50% of 5:5-diphenylbarbituric acid (I), about 12% of 4-hydroxybenzofuro-[2:3-*d*]-pyrimid-2(4*a*)-one (II), m.p. 351—353°, and 15—30% of other acids (A); a little $\text{CHPh}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ is produced [by hydrolysis and subsequent decarboxylation of (I)] during the isolation of the products. (II) undergoes slow hydrolysis (10% NaOH to NH_3 (2 mols.), CO_2 (2 mols.), and *o*-hydroxyphenyl-acetic acid (III), m.p. 148—149° (1 mol.). (II) probably results from the intermediate 5-hydroxy-5-phenylbarbituric acid by loss of H_2O and subsequent



acetic acid (III), m.p. 148—149° (1 mol.). (II) probably results from the intermediate 5-hydroxy-5-phenylbarbituric acid by loss of H_2O and subsequent

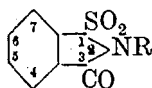
rearrangement. (III) is also prepared (diazo-method) from $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. A small amount of probably the SO_3H -derivative of (I) is isolated from (A); hydrolysis (10% NaOH) gives NH_3 , CO_2 , and a Na salt, $\text{C}_{14}\text{H}_{11}\text{O}_5\text{SNa}$ (? Na sulphodiphenylacetate). H. B.

Reactivity of arylacetamidopolymethylene compounds. T. OGATA (Proc. Imp. Acad. Tokyo, 1937, 13, 325—327).—A review. μ -Phenylacetamidovinylbenzoxazole ethiodide with methyl- and ethylmalonic acids gives respectively meso-methyl-, m.p. 217°, and ethyl-pentamethyleneoxacyanine methiodide, m.p. 220°. F. R. S.

Properties of isosteric and structurally similar compounds. III. Syntheses of 2:4-diketothiazolidines, geminally substituted in position 5, with narcotic properties. H. ERLÉNMEYER and H. VON MEYENBURG (Helv. Chim. Acta, 1937, 20, 1388—1393; cf. A., 1937, II, 216).—Treatment of $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}_2\text{Et}$ with saturated aq. NH_3 at room temp. and of the product with Na_2CO_3 in boiling H_2O affords 2:4:6-triketo-5:5-diethylpiperidine, m.p. 218°, which may be regarded as formed by replacement of the NH group of diethylbarbituric acid by the isosteric CH_2 group. It is acidic, sol. in NaHCO_3 , and does not give a coloration with FeCl_3 , $\text{CET}_2\text{Br}\cdot\text{CO}_2\text{H}$ is transformed by the successive action of $\text{CS}(\text{NH}_2)_2$ and Na_2CO_3 or conc. NH_3 into 2-imino-4-keto-5:5-diethylthiazolidine, m.p. 233.5° (corr.), hydrolysed by boiling 30% H_2SO_4 or conc. HCl to 2:4-diketo-5:5-diethylthiazolidine, b.p. 165°/14 mm., m.p. 76°; this with 2N-NaOH and MeI in MeOH affords 2:4-diketo-3-methyl-5:5-diethylthiazolidine, b.p. 118°/10 mm. $\text{CPr}_2\text{Br}\cdot\text{CO}_2\text{H}$ and $\text{CS}(\text{NH}_2)_2$ at 160° similarly yield 2-imino-4-keto-5:5-di-n-propylthiazolidine, m.p. 230° (corr.), hydrolysed to 2:4-diketo-5:5-di-n-propylthiazolidine, m.p. 72°. $\text{CPhEtBr}\cdot\text{CO}_2\text{H}$ and $\text{CS}(\text{NH}_2)_2$ at 100°/vac. afford α -phenylcrotonic acid and, after hydrolysis, 2:4-diketo-5-phenyl-5-ethylthiazolidine, m.p. 138.5°. 2-Imino-4-ketothiazolidine, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$, and NaOH give a product hydrolysed by boiling 30% H_2SO_4 to 2:4-diketo-5:5-diallylthiazolidine, m.p. 90.5°, which gives NH_3 but not $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$ when degraded by alkali. Certain of these substances resemble the dialkylbarbituric acids in their narcotic properties. H. W.

4-Methyl-5-p-hydroxyethylthiazole.—See B., 1937, 1316.

[Substituted saccharins.] **Chemical constitution and sweetness.** C. FINZI and M. COLONNA (Atti R. Accad. Lincei, 1937, [vi], 26, 19—24).—Et saccharin-2-carboxylate [*N*-carbethoxy-*o*-benzoisulphinide] (annexed formula) and *p*-phenetidine (I) yield saccharin-2-carboxyl-*p*-phenetidide, m.p. 156° (decomp.). 6-Amino-saccharin (II) and Ac_2O give the 2-Ac derivative, m.p. 261°, of 6-acetamidosaccharin, m.p. 284°, whilst Na aminosaccharinate and ClCO_2Et give 6-urethanosaccharin, m.p. 265°, and its Et 2-carboxylate, m.p. 203° (III). Diazotised (II) gives 6-hydroxysaccharin (IV), m.p. 264° (decomp.), very sweet; or, by coupling with



(II), 6-amino-5-(saccharin-6'-azo)saccharin, m.p. 241° (decomp.). 6-Salicylideneaminosaccharin has m.p. 276—277°. When fused with $\text{NH}_2\cdot\text{CO}_2\text{Et}$, (II) gives 6-carbamidosaccharin, no m.p. <305°. From (I) and (II), 6-(*p*-phenetylcarbamido)saccharin, m.p. 227—228°, is obtained. COCl_2 in presence of NPhMe_2 converts (II) into s-6:6'-disaccharinylcarbamide, no m.p. <300°. From (I) and (III), 6-(*p*-phenetylcarbamido)saccharin-2-carboxyl-*p*-phenetidide, m.p. 228—229°, is formed. None of these compounds, except (IV), is sweet. E. W. W.

Benzthiazyl disulphides.—See B., 1937, 1316.

Benzthiazole derivatives. I. 5-Benzthiazolyl-aminoacridines. N. S. DROZDOV (J. Gen. Chem. Russ., 1937, 7, 1668—1674).—1-Amino- or 4-bromo-1-amino-benzthiazole does not react with 5-phenoxyacridine, or with 3-methyl-, 3-methoxy-, or 2-chloro-5-phenoxy-7-methoxy-acridine (I), m.p. 154—156°. 5-(1'-Amino-4'-benzthiazolyl)amino-3-methyl-, m.p. 208—209°, -3-methoxy-, m.p. 268—269°, and -2-chloro-7-methoxy-acridine, m.p. 273—274°, are prepared from 1:4-diaminobenzthiazole and the appropriate 5-phenoxyacridine derivatives, in EtOH at the b.p. (I) is prepared by heating 2:5-dichloro-7-methoxyacridine with PhOH, and treating the 2-chloro-5:5-diphenoxy-7-methoxy-5:5-dihydroacridine hydrochloride, m.p. 243—244°, so formed with aq. NH_3 . R. T.

Constitution of mimosine. Substituted phenyl-aminoacetic acids. H. NIENBURG and K. TAUBÖCK (Z. physiol. Chem., 1937, 250, 80—86; cf. Renz, A., 1937, III, 50).—Mimosine, probably a β -dihydroxypyridylalanine $(\text{OH})_2\text{C}_5\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, m.p. 231°, yields a Cu salt, $\text{C}_8\text{H}_5\text{O}_4\text{N}_2\text{Cu} + 2\text{H}_2\text{O}$, and consumes 1 equiv. of NaOH. 3-Amino-*L*-tyrosine yields a Cu salt, $\text{C}_9\text{H}_{10}\text{O}_3\text{N}_2\text{Cu} + 2.5\text{H}_2\text{O}$. The Cu salts of tyrosine and dihydroxyphenylalanine contain only 1 equiv. of Cu. Salicylaldehyde with aq. NH_4Cl shaken for 5 hr. with aq. KCN yields a compound which, when boiled with HCl for 1 hr., evaporated to dryness, and treated with Ag_2O , gives 2-hydroxyphenylglycine, m.p. 204° (decomp.) [Cu salt, $(\text{C}_8\text{H}_5\text{O}_3\text{N})_2\text{Cu} + 2\text{H}_2\text{O}$]. Similarly 3-hydroxy-2-methoxybenzaldehyde yields 3-hydroxy-2-methoxyphenylglycine, $\text{C}_8\text{H}_{11}\text{O}_4\text{N} + \text{H}_2\text{O}$, m.p. 197° (decomp.), and Et 5-aldehydo-2-hydroxybenzoate yields 4-hydroxy-3-carboxyphenylglycine, $\text{C}_9\text{H}_9\text{O}_5\text{N} + 2\text{H}_2\text{O}$, decomp. 200° [(5- NO_2 -derivative, decomp. 195°]. 2:4-(OMe) $\text{C}_6\text{H}_3\cdot\text{CHO}$ suspended in EtOH and heated with aq. KCN and $(\text{NH}_4)_2\text{CO}_3$ for 20 hr. in CO_2 at 80°/15 atm. gives 2:5-dimethoxyphenylhydantoin, m.p. 175—176°, which yields 2:4-dimethoxyphenylglycine, m.p. 183—184° [(3- NO_2 -derivative, m.p. 162° (decomp.); NH_2 -derivative, m.p. 172° (decomp.), and its Cu salt, $(\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}_2)_2\text{Cu} + 4\text{H}_2\text{O}$], when boiled for 15 hr. with 20% aq. KOH. W. McC.

Minor alkaloids of Duboisia myoporoides. G. BARGER, W. F. MARTIN, and W. MITCHELL (J.C.S., 1937, 1820—1823).—Tigloidine (I), $\text{C}_{13}\text{H}_{21}\text{O}_2\text{N}$, a syrup, valeroidine (II), $\text{C}_{13}\text{H}_{23}\text{O}_3\text{N}$, m.p. 85°, $[\alpha]_D^{25} -9.0^\circ$ in EtOH, and base Z (III), $\text{C}_{12}\text{H}_{21}\text{O}_2\text{N}$, a syrup (oxalate, m.p. 285—290°; hydrobromide, m.p. 219—

220°), have been isolated in 0.1, 0.1, and 0.003% of the drug, respectively. The *hydrobromide*, m.p. 234—235° of (I) is reduced (PtO₂-H₂) to *dihydrocligloidine hydrobromide*, m.p. 186—187° (*methiodide*, m.p. 209°; *picrate*, m.p. 134.5°; *aurichloride*, m.p. 151°). (I) also forms a *methiodide*, m.p. 244—245°, *picrate*, m.p. 239°, *aurichloride*, m.p. 213.5—214°, and *Br₂-compound*, m.p. 187°. Hydrolysis of (I) gives tiglic acid and ψ -tropine, from which it can be synthesised. *Acetyl tropine hydrobromide* has m.p. 187—187.5°; and *acetyl- ψ -tropine hydrobromide* has m.p. 205°. Hydrolysis of (II) (*hydrobromide*, m.p. 170—172°, [α]_D²⁰ +5.0° in EtOH) affords Bu^oCO₂H and dihydroxytropine and is hence the *isovaleryl ester* of dihydroxytropine. F. R. S.

Sophora alkaloids. I. Alkaloids of the seeds of *S. microphylla*, Ait. L. H. BRIGGS and J. RICKETTS (J.C.S., 1937, 1795—1798).—From the crude alkaloid fraction (1—2.5% yield), *methyleytisine*, *matrine*, *cytisine*, a *base* (C₁₅H₂₃O₄N₃?), m.p. 293—296° (*picrate*, m.p. >370°), and a *base*, m.p. 168—171°, have been isolated. F. R. S.

Cinchona alkaloids in pneumonia. V. Alkyl ethers of *apocupreine*. C. L. BUTLER, (MISS) M. HOSTLER, and L. H. CRETCHER (J. Amer. Chem. Soc., 1937, 59, 2354—2355).—*apoCupreine* and the appropriate alkyl *p*-toluenesulphonate give the *Pr^a*, m.p. 169°, [α] -197° (*dihydrochloride*, [α] -240°), *Pr^b*, m.p. 133°, [α] -185° (*dihydrochloride*, [α] -234°), *Bu^a*, m.p. 161—163°, [α] -180° (*dihydrochloride*, [α] -236°), *Bu^b*, m.p. 180°, [α] -183° (*dihydrochloride*, [α] -234°), and *Bu^c*, amorphous (2:1 *sulphate*, [α] -156° in EtOH), *ethers*. [α] of the salts are in H₂O, but of the bases in EtOH. The ethers have strong action against pneumococcus, but their toxicity to mice is > that of the Et ether. The *Pr* ethers cause visual disturbance in dogs. R. S. C.

Ergocristine and ergocristinine, alkaloids from ergot. A. STOLL and E. BURCKHARDT (Z. physiol. Chem., 1937, 250, 1—6).—Ergot yields a *compound* (I), m.p. 172—175° (decomp.), [α]_D²⁰ +105° in CHCl₃, decomposed by MeOH or HCl in EtOH into 1 mol. of *ergosinine* (II) and 1 mol. of *ergocristine* (III), C₃₅H₃₉O₅N₅, m.p. 155—157° (decomp.), [α]_D²⁰ -183° in CHCl₃ (*hydrochloride*, [α]_D²⁰ +105.7° in abs. EtOH; *phosphate*; *tartrate*). When boiled for 2 hr. with MeOH (III) gives the isomeric *ergocristinine*, m.p. 214° (decomp.), [α]_D²⁰ +366° in CHCl₃, reconverted into (III) by boiling with 1% H₃PO₄ in EtOH. When equal amounts of (II) and (III) in EtOAc are mixed (I) is produced. W. McC.

Racemic lysergic acid. Resolution into the optical antipodes. A. STOLL and A. HOFMANN (Z. physiol. Chem., 1937, 250, 7—10).—Ergot alkaloids hydrolysed with N₂H₄.H₂O give the racemic *hydrazide* (I), C₁₆H₁₈ON₄, m.p. 240° (decomp.), of *isolysergic acid*. With conc. aq. KOH (I) gives racemic *lysergic acid*. (II) [+H₂O, m.p. 240—250° (decomp.)] and with HNO₂ racemic *isolysergic azide* (III), which, with aq. NaHCO₃, gives racemic *isolysergic acid* [+H₂O, m.p. 240—245° (decomp.)]. The compound C₂₅H₂₇O₂N₃ of (III) with *l*-norephedrine was resolved by EtOH-Et₂O into the com-

pound (IV), C₂₅H₂₇O₂N₃ + Et₂O, m.p. 125—130° (decomp.), [α]_D²⁰ -267° in COMe₂, and the *compound* (V), C₂₅H₂₇O₂N₃, [α]_D²⁰ +296° in COMe₂. Vigorous alkaline hydrolysis of (IV) and (V) yields *l*- (VI) and *d*-lysergic acid, m.p. 235—240°, [α]_D²⁰ \pm 40° in C₅H₅N, respectively; (VI) crystallises from H₂O with 1 H₂O. W. McC.

Morphine ethers.—See B., 1937, 1408.

Identity of solanecarpine with solanine-s. L. H. BRIGGS (J. Amer. Chem. Soc., 1937, 59, 2467—2468).—Solanecarpine from *Solanum xanthocarpum* and solanine-s (I) from *S. sodomaeum* or *S. auriculatum* are identical (mixed m.p.). Analyses support the formulæ C₄₄H₇₅O₁₈₋₁₉N for (I) and C₂₆H₄₃O₃N for solanidine-s. R. S. C.

Alkaloids of *Veratrum album*. II. The individual alkaloids and their relationships to one another. Protoveratridine, germerine, and protoveratrine. W. POETHKE (Arch. Pharm., 1937, 275, 571—599; cf. A., 1937, II, 394).—Protoveratridine (I) (best purified by gradual addition of NH₃ to a hot solution of the crude alkaloid in AcOH-EtOH), m.p. 266—267° (corr.), is shown by analysis and determination of mol. wt. to be C₃₁H₄₉O₉N. It yields a *platinichloride*, decomp. 195—200°, (also +7H₂O or +2EtOH.3H₂O), *aurichloride* which becomes discoloured >150°, *hydrochloride*, m.p. 243—245° (corr.; decomp.) after slight discoloration, and a *picrate* decomp. 244—246°. It is hydrolysed by KOH-MeOH to *l*-CHMeEt.CO₂H and *germine* (II), C₂₆H₄₁O₈N, m.p. about 220° after softening at 160—170°, [α]_D²⁰ +21.1° in dil. AcOH, or (as *monohydrate*) [α]_D²⁰ +4.9° in EtOH (also +CHCl₃, +3CHCl₃, +2MeOH, +EtOH, +3H₂O), which gives an *aurichloride*, *picrate*, m.p. 190—205° (decomp.) after softening at about 175°, *picrolonate*, and an *amine-oxide*, C₂₆H₄₁O₉N, m.p. 249° (corr.; decomp.). It contains 5 OH (Zerevitinov) but is free from CH₂O₂. (II) is therefore C₂₆H₃₆O₃N(OH)₅ and (I) is (OH)₄C₂₆H₃₆O₃N.CO₂.CHMeEt. The very hygroscopic germerine (III) (also +1H₂O), [α]_D²⁰ +10.8° in CHCl₃, is C₃₆H₅₇O₁₁N. It gives an *aurichloride*, decomp. 153° (corr.), *hydrochloride*, m.p. 215° (corr.; decomp.) (also +2H₂O), *hydrobromide* (also +2H₂O), m.p. 212—213° (corr.; decomp.), *hydrothiocyanate monohydrate*, m.p. 221—223° (corr.; decomp.), *H sulphate*, and *picrate* (also +1H₂O), m.p. 186—187° (corr.; decomp.) after softening. It is hydrolysed by KOH-EtOH to *l*-CHMeEt.CO₂H, OH.CMeEt.CO₂H, and (II). It is converted by Ba(OH)₂ into (I). Therefore (III) is (OH)₃.C₂₆H₃₆O₃N { CO₂.CHMeEt / CO₂.CMeEt.OH. Protoveratrine (IV), m.p. 255—256° (corr.; decomp.), [α]_D²⁰ -9.1° in CHCl₃, is C₄₀H₆₃O₁₄N. It gives an *aurichloride* (also +1H₂O), decomp. 199° (corr.), *hydrochloride monohydrate*, m.p. 234—236° (corr.; decomp.), *hydrobromide trihydrate*, m.p. 230—232° (corr.; decomp.), *hydriodide* (+2.5H₂O), m.p. 247—248° (corr.; decomp.), *hydrothiocyanate* (also *dihydrate*), m.p. 221—223° (corr.; decomp.), and *picrate*, m.p. 216—220° (corr.; decomp.). It is hydrolysed by KOH-EtOH to AcOH, *l*-CHMeEt.CO₂H, OH.CMeEt.CO₂H, and *protoverine*, C₂₈H₄₅O₁₀N (*picrolonate*; *picrate*). (IV) is a *tert.* base which contains

5 active H. (Zerevitinov) but not OMe, or CH_2O_2 . It is probably $(\text{OH})(\text{OAc})\text{C}_{28}\text{H}_{41}\text{O}_6\text{N}(\text{CO}_2\cdot\text{CHMeEt})\cdot\text{CO}_2\cdot\text{CMeEt}\cdot\text{OH}$. Since (II) does not react with CH_2N_2 it does not contain phenolic OH. MeI is added in MeOH or CHCl_3 but the quaternary methiodide is not homogeneous. With CNBr only the hydrobromide of (II) is produced. Oxidation of acetylated (II) by CrO_3 in AcOH occurs only in presence of H_2O and appears to lead to complete oxidation of part of the material. Rehydrogenation by $\text{Hg}(\text{OAc})_2$ occurs slowly and after separation of HgOAc ($=2\text{H}$) a brown syrup results. H. W.

p-Arsenated mixed ethers. P. O. BARE and C. S. HAMILTON (J. Amer. Chem. Soc., 1937, 59, 2444—2446).— $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ (I) and $\text{OH}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$ in aq. NaOH give 30% of $\alpha\gamma$ -di-*p*-arsinophenoxypropan- β -ol, m.p. $>270^\circ$, which with HNO_3 (d 1.5) and conc. H_2SO_4 at 0° affords the β -nitrate, decomp. 218° , of $\alpha\gamma$ -di-(2-nitro-4-arsinophenoxy)propan- β -ol (II), decomp. 260° . (II) is reduced (H_2 , Raney Ni, aq. NaOH) to $\alpha\gamma$ -di-(2-amino-4-arsinophenoxy)propan- β -ol, decomp. 186° (Na_2 salt). (I) and $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ in aq. NaOH give 55—60% of 4- $\beta\gamma$ -dihydroxy-*n*-propoxyphenylarsinic acid (III), m.p. $>250^\circ$ (Na salt), which with HNO_3 (d 1.5) and conc. H_2SO_4 at 10° affords the $\beta\gamma$ -dinitrate (IV), m.p. $132\text{—}133^\circ$, of 3-nitro-4- $\beta\gamma$ -dihydroxy-*n*-propoxyphenylarsinic acid (V), m.p. $>250^\circ$ (Na salt). (V) is reduced catalytically to the 3- NH_2 -derivative (VI), m.p. $194\text{—}196^\circ$ (decomp.) (Na salt). Reduction of (III), (V), and (VI) with H_2SO_3 + a little HI gives 4- $\beta\gamma$ -dihydroxy-*n*-propoxyphenylarsenious oxide, m.p. $122\text{—}123^\circ$, and its 3- NO_2 , m.p. $167\text{—}168^\circ$, and 3- NH_2 , m.p. $>250^\circ$, -derivatives, respectively; reduction with H_3PO_2 affords 4 : 4'-di-($\beta\gamma$ -dihydroxy-*n*-propoxy)arsenobenzene, m.p. $164\text{—}165^\circ$, and its 3 : 3'-(NO_2) $_2$, m.p. $197\text{—}198^\circ$ [tetranitrate, m.p. $98\text{—}99^\circ$, similarly obtained from (IV)], and 3 : 3'-(NH_2) $_2$, m.p. $170\text{—}173^\circ$ (decomp.), -derivatives, respectively. H. B.

Derivatives of acetophenone-*p*-arsinic acid. P. G. SERGEEV and D. G. KUDRJASHEV (J. Gen. Chem. Russ., 1937, 7, 1488—1494).—Diazotised $p\text{-C}_6\text{H}_4\text{Ac}\cdot\text{NH}_2$ (I) and AsCl_3 in MeOH give $p\text{-C}_6\text{H}_4\text{Ac}\cdot\text{AsO}(\text{OH})_2$ (II), a solution of which in conc. HCl is saturated with SO_2 at 100° for 2 hr., to yield *p*-acetophenonedichloroarsine (III), m.p. 100° , b.p. $202^\circ/13\text{—}15$ mm. This is chlorinated in EtOH solution at 40° , and the product is hydrolysed, to yield ω -chloroacetophenone-*p*-arsinic acid, m.p. $189\text{—}190^\circ$ (decomp.), from which ω -chloroacetophenone-dichloroarsine, m.p. $56\text{—}57^\circ$, is prepared as above. (II) and isatin are heated in 33% KOH at $150\text{—}160^\circ$ (7 hr.), to yield atophan-4-arsinic acid, not melting at 225° . When treated with hot aq. NaOH (III) yields $p\text{-C}_6\text{H}_4\text{Ac}\cdot\text{AsO}$ (IV). Diazotised (I) and (IV) afford bis-(*p*-acetophenone)arsinic acid, m.p. $185\text{—}186^\circ$, converted as above into di-*p*-acetophenonechloroarsine, m.p. $124\text{—}125^\circ$. R. T.

Mercuryphenyl chromates.—See B., 1937, 1409.

Preparation of mercury organic compounds by direct action of metallic mercury. A. E.

KRETOV and V. A. ABRAMOV (J. Gen. Chem. Russ., 1937, 7, 1572—1578).— $\text{CHPhBr}\cdot\text{CN}$ in COMeEt and Hg (8 hr. at 40°) yield a mixture of phenylbromomercuriacetonitrile, m.p. 157° , and of its decomp. product, dicyanodibenzyl, m.p. 237° . R. T.

Arylmercury salts of hydroxy-aromatic acids.—See B., 1937, 1408.

Proteins. V. Acetylated proteins. A. KIZEL, Z. KAIPOVA, and Z. SOSINA (Biochimia, 1937, 11, 713—719).—Acetylation of edestin and cucurbitin at 0° in $\text{C}_5\text{H}_5\text{N}$ and 10% NaHCO_3 gave Ac derivatives, which were hydrolysed at 0° with 0.1N-NaOH; only the *O*-Ac groups being removed. Colour reactions showed that the guanidine ring in arginine, the glyoxaline ring in histidine, and the indole ring of tryptophan were free, whilst the OH of tyrosine was acetylated. J. N. A.

Reactions of furan compounds. VIII. Displacement of furfuraldehyde by aldehydes and its use in the determination of formaldehyde and acetaldehyde. V. V. TSCHELINCEV and E. K. NIKITIN (Bull. Soc. chim., 1937, [v], 4, 1727—1734).—Difurfurylideneacetone (I) in 60% H_2SO_4 is violet-red; on addition of CH_2O (or MeCHO), furfuraldehyde and divinyl ketone (or dipropenyl ketone) are formed, and the colour vanishes. CH_2O or MeCHO is determined by measuring colorimetrically the diminution of the concn. of (I) in a standard solution in a standard time, in comparison with a standard solution of aldehyde. The rate of disappearance of colour is \propto the concn. of aldehyde. J. D. R.

Phenothiazine. I. Colorimetric method for determination of phenothiazine. C. W. EDDY and F. DEEDS (Food Res., 1937, 2, 305—309).—Aq. Br is added to phenothiazine (I) in EtOH and the red coloration produced (believed to be due to 3 : 9-dihydroxyphenazothionium bromide) is determined colorimetrically. The method is applied to the determination of (I) in spray residues on apples. E. C. S.

Fluorescence in microchemistry: thalleioquinine reaction in ultra-violet light. M. HAITINGER (Mikrochim. Acta, 1937, 1, 1—4).—Addition of Br water to a solution of quinine (I) causes an initial brightening and then extinction of the blue fluorescence. Addition of aq. NH_3 then causes the appearance of yellow-green fluorescence. The reaction may be carried out as a spot test on filter-paper, best by exposure of a drop of aq. (I) to the vapours of Br and aq. NH_3 . 0.0004 mg. of (I) may be so detected; quinidine, but no alkaloid of other groups, also gives the reaction. J. S. A.

"Sulphomorphid" and the purple fluorescence test for morphine. C. C. FULTON (J. Amer. Pharm. Assoc., 1937, 26, 726—729).—Morphine (I) with H_2SO_4 at 40° for approx. 1 hr. yields a cryst. "sulphomorphid" [probably apomorphine-sulphonic acid (Kitasato and Goto, A., 1931, 105)] insol. in H_2O but sol. in aq. NH_3 to a fluorescent solution. This is suggested as a test for (I). With H_2SO_4 at 90° (I) yields a H_2O -sol. derivative. Codeine and dionine react similarly to (I). F. O. H.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

FEBRUARY, 1938.

Review of work in organic chemistry in the U.S.S.R. during the past 20 years. I. F. BOGDANOV (J. Appl. Chem. Russ., 1937, 10, 1784—1804).—A review. R. T.

Mechanism of the reaction of substitution and Walden inversion. II. P. A. LEVENE, A. ROTHEN, and M. KUNA (J. Biol. Chem., 1937, 121, 747—759).—From a comparison of the first and second partial rotations, and the rotation in the visible region, of substances of type $\text{CHRM}\cdot\text{CH}_2\text{X}$ ($\text{X} = \text{halogen}, \text{N}_3, \text{SH}, \text{OH}, \text{NH}_2, \text{or } \text{SO}_3\text{H}$) with those of the acids $\text{CHRX}\cdot\text{CO}_2\text{H}$ as correlated by the two following rules, Levene's "rule of shift" (ascribing identical configurations to α -carboxylic acids of which α changes in the same direction when passing from the undissociated to the ionised state) is now abandoned in favour of the rule that every substitution reaction (including replacement of halogen by N_3) of normal saturated aliphatic compounds is connected with a change of configuration. The configurative relations of substances of type $\text{CHRR}'\text{X}$ are also discussed, with the same conclusion. Accordingly the configurative relationship of *sec.* carbinols of the corresponding halides, and of α -hydroxy- and α -halogeno-carboxylic acids, as formulated by Clough (A., 1926, 111, 937), by Levene and Mikeska (A., 1927, 1171; 1928, 170), and by Levene and Rothen (A., 1936, 1051; 1937, II, 2, 316) are abandoned in favour of those advocated by Freudenberg (A., 1928, 153, 535; 1935, 849) and by W. Kuhn (A., 1930, 276).

Rotatory dispersion data for (+)- β -thiol-butane and -octane, and for (+)- α -thiol- β -methylbutane and - γ -methylpentane, are tabulated and discussed, as are those for (—)-Na and (—)-Me octane- β -sulphonate and (+)-Na β -methylbutane- and (+)-Me β -methylhexane- α -sulphonate. E. W. W.

Structure of organic compounds. V. N. UFIMTSEV (J. Gen. Chem. Russ., 1937, 7, 1874—1877).—Polemical against Dubrovai (cf. A., 1937, I, 348). R. T.

Catalytic cyclisation of aliphatic compounds. II. Cyclisation and dehydrogenation of hydrocarbons with oxide and sulphide catalysts. B. MOLDAVSKI, G. KAMUSCHER, and M. KOBILSKAJA. III. Cyclisation and dehydrogenation of hydrocarbons with different charcoals. B. MOLDAVSKI, F. BEZPROZVANNAJA, G. KAMUSCHER, and M. KOBILSKAJA (J. Gen. Chem. Russ., 1937, 7, 1835—1839, 1840—1847).—II. Dehydrogenation of cyclohexane (I) and cyclisation of *n*-octane (II) are catalysed by the same substances (TiO_2 , MoO_3 , MoS_2 , and ZnO), at 450—550°; SiO_2 and glass are without effect in either reaction.

O^* (A., II.)

III. Active C catalyses both dehydrogenation of (I) and cyclisation of (II) and of Bu^β_2 , at 500—560°.

R. T.

Thermal decomposition of dodecane, $\beta\beta$ -trimethylpentane, and $\beta\epsilon$ -dimethylhexane. Kinetics of decomposition of ethane at reduced pressures.—See A., I, 35.

Mechanism of halogenation of phenols. I. Reaction of benzenesulphondichloroamide with phenol in presence of olefines. M. V. LICHOSCHERSTOV and R. A. ARCHANGELSKAJA (J. Gen. Chem. Russ., 1937, 7, 1914—1928).— PhOH in CCl_4 , $(\text{CHMe})_2$ (I), and $\text{PhSO}_2\cdot\text{NCl}_2$ (II) at -15° , followed by extraction with 3% NaOH and distillation of the residual CCl_4 solution, yield two diastereoisomerides, m.p. 83° and 115.8° , of β -chloro- γ -benzenesulphonamido-*n*-butane (III), yielding, respectively, trans-, m.p. 77° , and cis-2:3-dimethyl-*N*-benzenesulphonylethyleneimine, m.p. 42° , when treated with NaOH - EtOH at room temp. In addition PhOCl is formed in the original reaction, and this reacts with (I) to give β -chloro- γ -phenoxybutane (IV), b.p. $120^\circ/20$ mm. The entire process is represented: $\text{PhOH} + (\text{II}) \rightarrow \text{PhOCl} + \text{PhSO}_2\cdot\text{NHCl}$ (V); $\text{PhOCl} + (\text{I}) \rightarrow (\text{IV})$; $(\text{V}) + (\text{I}) \rightarrow (\text{III})$. The corresponding products obtained with *o*- or *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ in place of PhOH are: (III), β -chloro- γ -*o*-, b.p. 145 — $148^\circ/20$ mm., and *p*-chlorophenoxybutane, b.p. $118.5^\circ/5$ mm., whilst with $\text{CHET}\cdot\text{CH}_2$ in place of (I) the products with PhOH are α -chloro- β -phenoxybutane, b.p. 121.5 — $122.5^\circ/2$ mm., *N*-benzenesulphonylethylethyleneimine, m.p. 76° , and α -chloro- β -benzenesulphonamidobutane, m.p. 83.5° , and with $\text{CMe}_2\cdot\text{CH}_2$ α -chloro- β -phenoxy-, b.p. 118 — $119^\circ/20$ mm., and α -chloro- β -benzenesulphonamido- β -methylpropane, m.p. 76° , together with a mixture of chloroisobutanes, of which $\text{CH}_2\text{Cl}\cdot\text{CMe}\cdot\text{CH}_2$ is identified. R. T.

Measurement of olefine formation from alkyl bromides. Mechanism of substitution and olefine reactions with alkyl halides. W. TAYLOR (J.C.S., 1937, 1962—1967; cf. A., 1937, II, 182).—Olefine formation at 25° and 55° from EtBr , Pr^βBr , $\text{Bu}^\gamma\text{Br}$, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$ (I), and CHPhMeBr has been measured in H_2O , EtOH , and CCl_4 alone, and in solutions in dry EtOH with varying $[\text{NaOEt}]$. Yields of olefine increase in the order primary, *sec.*, *tert.*-bromides and with higher temp. and $[\text{NaOEt}]$. At any temp. [except with (I)] the concn. effect has an upper limit, probably owing to NaOEt mols. being more active in olefine formation than OEt' ions. (I) at 55° alone or in dry EtOH gives no olefine but at $[\text{NaOEt}]$ not below 0.05N , it yields about 90% of olefine, probably due to OEt' ions. Yields in solvents

alone show that EtOH (basic) may have considerable effect, H₂O very little effect, and CCl₄ (non-basic) no effect, on olefine formation. Heating of bromides alone at 25° or 55° gives small yields of olefine. Hence possible reagents in olefine formation are OEt⁺ ions, NaOEt mols., solvents, and the bromides themselves.

Substitution and olefine reactions of alkyl halides CH₂R·CH₂·Hal. through the agency of (1) anions (B') or (2) unionised mols. (AB) are discussed. In case (1) substitution results from electron transfer B' → α-C atom, and olefine formation from B' → β-H atom. The proportion of olefine formation is therefore determined by basic strength of B', by sizes of positive charges on α-C and β-H, and by polarisability of Hal., since increase of this induces increased positive charge on β-H relative to α-C. In both reactions the transfer α-C → Hal. must occur before completion. Hence substitution will be preferred, since Hal. is more remote from β-H than from α-C. In case (2) substitution results from transfers Hal. → A and B → α-C, and olefine formation from transfers Hal. → A and B → β-H. When Hal. is not partly bound by α-H, as in *tert.*-halides, it is freer to react with A. B therefore acquires more electron-donating power, *i.e.*, becomes a stronger base, and olefine formation is preferred and increases along the series primary, *sec.*-, *tert.*-halides, with increasing [AB], and with increasing strength of base. Substitution of I for Br or of Br for Cl will also affect olefine formation through increased polarisability of Hal. and change in reactivities of α-C and β-H. The accelerating effects of H₂O and of ionic base on reaction rates of CH₂R·CH₂·Hal. in EtOH-H₂O are also explained on this basis.

E. G. B.

Kinetics and mechanism of transformations of unsaturated hydrocarbons. VI. Polymerisation of propylene under pressures greater than atmospheric. S. P. MITZENGENDLER (J. Gen. Chem. Russ., 1937, 7, 1848—1857).—The process of polymerisation of CHMe·CH₂ is catalysed by Fe at 480°, but not at 600°, at which temp. catalytically active solid C compounds are formed. At 480° the initial products are dimethylcyclobutane and *n*- or *iso*-hexanes, whilst at 600° a mixture of CH₄, C₂H₄, and C₆H₁₀ is obtained. The highest yield of liquid polymerides, b.p. <150°, is obtained at 520°, in a Cu reactor, and at >40 atm. pressure, with >50% conversion of CHMe·CH₂.

R. T.

Oxidation velocities of alkenes with peracetic acid.—See A., I, 36.

Thermal reactions of unsaturated hydrocarbons. IV. Cracking of mixtures of propylene with butadiene and isobutylene at atmospheric pressure. V. G. MOOR and N. V. STRIGALEVA. **V. Kinetics and mechanism of thermal transformations of diisobutylene at atmospheric pressure.** V. G. MOOR and L. V. SCHILAEVA (J. Gen. Chem. Russ., 1937, 7, 1766—1778, 1779—1786).—IV. CH₂:CHMe (I) and CH₂:CMe₂ react at the same rate to give the same products, whether heated alone or together at 600°, whilst in (I)-(CH₂:CH·)₂ (II) mixtures the velocity of transformation of (I) is increased to an extent α concn. of (II).

V. The yields of products of pyrolysis of

CH₂:CMe·CH₂Bu'·CMe₂:CHBu' mixtures at 490—640° are as would be expected from Rice's theory (A., 1931, 819).

R. T.

Velocity of hydrogenation of isomeric hexenes. S. P. LAGEREV and S. F. BABAK (J. Gen. Chem. Russ., 1937, 7, 1661—1663).—The velocities of hydrogenation (Pt catalyst) of CHBu':CH₂, CHBu':CH₂, CMeEt:CHMe, and CMe₂:CHEt are as 33 : 70 : 144 : 240.

R. T.

Action of aromatic diazo-compounds on unsaturated compounds. I. A. P. TERENCEV. **II. Sensitive reaction for divinyl.** A. P. TERENCEV and E. M. IVANOVA (J. Gen. Chem. Russ., 1937, 7, 2026—2027, 2028—2029).—I. Theoretical.

II. *p*-C₆H₄(NH₂)₂ is diazotised at < -5°, and 2 ml. of the solution are added to 8 g. of ice and 2 ml. of AcOH, at -15°. The gas under analysis is passed into the mixture, when a deep yellow to red coloration appears in presence of dienes.

R. T.

Course of polymerisation of pure olefines. F. JOSTES and W. BARTELS (Oel u. Kohle, 1937, 13, 1166—1172).—Heptene (I) does not polymerise when treated with ZnCl₂, SnCl₄, or H₂SO₄. Treatment of (I) in hexane with AlCl₃ gives a mixture from which a definite polymeride could not be isolated. Di- and tri-polymerides of the C₇ to C₁₂ olefines are formed by heating them at 80—90° in the presence of P₂O₅. These are strongly branched olefines, the exact structure of which has not yet been determined; it is such as to inhibit further polymerisation under the same experimental conditions. Propylene in the presence of P₂O₅ is polymerised to oils, mainly of b.p. 125—150°, but including also those boiling in the lubricating oil range; di-polymerides could not be isolated from the product.

A. B. M.

Isomerisation of allene hydrocarbons by silicates. V. Isomerisation of *tert.*-butylallene. J. M. SLOBODIN (J. Gen. Chem. Russ., 1937, 7, 1664—1667).—CHBu':C:CH₂ is rearranged to CMe₂:C:CMe₂ when passed over floridin at 230°.

R. T.

Constitution of lycopene and configuration of 6 : 7-dimethyl-9-*d*-arabitylisoalloxazine. P. KARRER (Ber., 1937, 70, [B], 2565—2566; cf. A., 1937, II, 378).—Reply is made to Kuhn and Grundmann (*ibid.*, 438) with regard to the constitution of lycopene and to Kuhn and Weygand (*ibid.*, 233) with respect to the configuration of 6 : 7-dimethyl-9-*d*-arabitylisoalloxazine.

H. W.

Photochemical oxidation of trichloroethylene to dichloroacetyl chloride by chlorine.—See A., I, 39.

Aliphatic chloro-derivatives. XI. Chlorination of isopentane to dichlorides. M. DAVIDOVA, Z. PAPIKINA, and D. TISCHTSCHENKO. **XII. Action of chlorine on *n*-pentane.** A. LEMKE and D. TISCHTSCHENKO (J. Gen. Chem. Russ., 1937, 7, 1992—1994, 1995—1998).—XI. Chlorination of liquid isopentane at 20°, or of the vapour at 115°, yields βγ-, βδ-, and αδ-dichloro-β-methylbutane.

XII. *n*-Pentane and Cl₂ at 20° afford βγ-, αβ-, αδ-, and probably αε-dichloropentane.

R. T.

Elimination of hydrogen bromide from saturated bromohydrins in presence of metallic catalysts. I. Elimination of hydrogen bromide from isobutylene bromide in presence of nickel, zinc, aluminium, and copper. N. I. MATUSEVITSCH (J. Gen. Chem. Russ., 1937, 7, 1909—1913).—An inseparable mixture of products is obtained when $\text{CMe}_2\text{Br}\cdot\text{CH}_2\text{Br}$ is passed over Ni at 500° , or Zn at $400\text{--}500^\circ$, pointing to profound structural changes in the mol. In presence of Al at $275\text{--}325^\circ$ gaseous and sooty products are obtained. The chief products with Cu at 420° were isobutenyl bromide, b.p. $93.5\text{--}94.5^\circ$, and some Bu^iBr . R. T.

Photochemical decomposition of aliphatic alcohols in aqueous solution.—See A., I, 39.

Catalytic dehydration of ethyl alcohol by alumina.—See A., I, 37.

Addition of hypochlorous acid to Δ^{β} -butene- $\alpha\delta$ -diol.—See A., I, 36.

Reactions relating to carbohydrates and polysaccharides. LIV. Surface tension constants of the polyethylene glycols and their derivatives. LV. Vapour pressures of the polyethylene glycols and their derivatives. A. F. GALLAUGHER and H. HIBBERT (J. Amer. Chem. Soc., 1937, 59, 2514—2521, 2521—2525).—LIV. γ and d for mono- to hepta-ethylene glycols are measured over a range of about 100° . The series const. for the total surface energy, 72 ± 1 ergs, is attained with triethylene glycol and closely approaches the val. 73.2 for $(\text{CH}_2)_2\text{O}$. Therefore, the glycols are probably oriented at the surface in a U-form, with $\text{CH}_2\cdot\text{O}\cdot\text{CH}_2$ at the surface; the OH group plays little part. The abnormally low val., 68.96 , of $(\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{O}$ (I) indicates spatial proximity of the two OH groups. Continuous increase in the Ramsay and Shields const. and in the difference between the calc. and observed vals. of $[P]$ with increasing mol. wt. indicate an abnormal factor, possibly partial orientation at the surface. The observed $[P]$ is low for $(\text{OH}\cdot\text{CH}_2)_2\text{O}$ and (I), but thereafter becomes increasingly high; the latter, abnormal deviation may be due to intramol. coordination, $\rightarrow \text{H}\cdot\text{O} \rightarrow \text{H}\cdot\text{O} \rightarrow$. Mol. vols. show large negative anomalies, best explained by zig-zag chains.

LV. V.p. of mono-, di-, tri-, and tetra-ethylene glycol and some allied compounds are determined and the mol. latent heat and Trouton's const. are calc. Certain abnormalities are noted. Initial decomp. temp. are shown to rise with the chain length; replacement of OH by Cl or OMe decreases the stability. R. S. C.

***n*-Propyl esters of pyrophosphorous, hypophosphoric, and pyrophosphoric acids, and the chloride of di-*n*-propylphosphorous acid.** A. E. ARBUSOV and A. I. RAZUMOV (J. Gen. Chem. Russ., 1937, 7, 1762—1765).— $\text{NaPr}^a_2\text{PO}_3$ (I) and Br in light petroleum yield a mixture of $\text{Pr}^a_4\text{P}_2\text{O}_5$ (II), b.p. $147.5\text{--}149^\circ/6$ mm., $\text{Pr}^a_4\text{P}_2\text{O}_6$, b.p. $167\text{--}170^\circ/3$ mm., and $\text{Pr}^a_4\text{P}_2\text{O}_7$, b.p. $178\text{--}179.5^\circ/4$ mm. (II) with H_2O yields $\text{Pr}^a_2\text{HPO}_3$. $\text{PCl}_2\cdot\text{OPr}^a$ and NaOPr^a in Et_2O afford $\text{PCl}(\text{OPr}^a)_2$, b.p. $65.5\text{--}66.5^\circ/8$ mm., which with (I) gives (II). R. T.

Syntheses of glycerophosphatidic acids and of glycerophosphatides. P. E. VERKADE and J. VAN DER LEE (Proc. K. Akad. Wetensch. Amsterdam, 1937, 40, 858—864).—Theoretical; a review of the literature (cf. A., 1937, II, 439). E. W. W.

Isolation and synthesis of glucose-1-phosphoric acid. C. F. CORI, S. P. COLOWICK, and G. T. CORI (J. Biol. Chem., 1937, 121, 465—477).—Glucose-1-phosphoric acid (I) (A., 1936, 1533), $[\alpha]_D^{25} + 118^\circ$ in H_2O , is obtained free from the 6-ester (II) by treating an extract of rabbit muscle (dialysed to remove Mg^{++}) with glycogen, adenylic acid, and a phosphate buffer of p_H 7, and preparing the Ba salt. $\text{C}_6\text{H}_{11}\text{O}_5(\text{PO}_4)\text{Ba}\cdot 3\text{H}_2\text{O}$, $[\alpha]_D^{25} + 75.5^\circ$ in H_2O . Unlike (II), (I) is non-reducing; it is hydrolysed by $\text{N}\cdot\text{H}_2\text{SO}_4$ at 100° , or by intestinal phosphatase, to glucose and inorg. phosphate. Synthetic (I), from α -1-bromotetra-acetylglucose and Ag_3PO_4 , and hydrolysis of the resulting *tris*(tetra-acetylglucose-1)-phosphoric acid, $[\alpha]_D^{25} + 122^\circ$ in MeOH, by $0.2\text{N}\cdot\text{MeOH}\cdot\text{HCl}$, at 25° for 16 hr., is identical in properties with natural (I). The velocity coeff. of hydrolysis by $1.25\text{N}\cdot\text{HCl}$ at 37° is 1.30×10^{-3} ; apparent dissociation consts. are $pK_1' = 1.1$, $pK_2' = 6.13$. The accelerating effect of Mg^{++} on the conversion of (I) into (II) is studied (cf. A., 1937, III, 306). E. W. W.

Thermal decomposition of dimethyl sulphite.—See A., I, 35.

Sulphur studies. XIII. Identification of aliphatic sulphonic acids. P. H. LATIMER and R. W. BOST. **XIV. Derivatives of higher mercaptans.** D. FORE, jun., and R. W. BOST (J. Amer. Chem. Soc., 1937, 59, 2500—2501, 2557—2558; cf. A., 1937, II, 456).—XIII. The following $\text{NHPh}\cdot\text{NH}_2$ salts are suitable for identifying the acids: *methane-*, m.p. $193.5\text{--}194^\circ$ (decomp.), *ethane-*, m.p. 182.8° , *propane- α -*, m.p. 204.5° (decomp.), *butane- α -*, m.p. $114\text{--}115^\circ$, *pentane- α -*, m.p. $108\text{--}108.2^\circ$, *hexane- α -*, m.p. $101\text{--}101.6^\circ$, *heptane- α -*, m.p. $100\text{--}100.5^\circ$, and *octane- α -sulphonate*, m.p. $90\text{--}90.5^\circ$. They can be titrated with $0.01\text{N}\cdot\text{NaOH}$. Large depressions of the m.p. are given by sulphonates differing by >1 CH_2 , small depressions by those differing by 1 CH_2 . $1:2:4\text{-C}_6\text{H}_4\text{Cl}(\text{NO}_2)_2$, NH_2Ph , $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br}$, and $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ are not suitable for identification of the acids.

XIV. The following are prepared. *Pb n-tri-*, m.p. 100° (97°), *-tetra-*, m.p. $104\text{--}105^\circ$ (99°), *-hexa-*, m.p. $106\text{--}107^\circ$ (99°), *-hepta-*, m.p. $108\text{--}109^\circ$ (100°), *-octa-*, m.p. $110\text{--}111^\circ$ (106°), and *-nona-decylmercaptide*, m.p. $112\text{--}114^\circ$ (108°), temp. in parentheses being those of initial darkening. $2:4\text{-Dinitrophenyl n-tri-}$, m.p. $94\text{--}94.5^\circ$, *-tetra-*, m.p. $93.5\text{--}94^\circ$, *-hexa-*, m.p. $95.5\text{--}96^\circ$, *-hepta-*, m.p. $98.5\text{--}99^\circ$, *-octa-*, m.p. $97\text{--}97.5^\circ$, and *-nona-decyl sulphide*, m.p. $99.5\text{--}100^\circ$. $2:4\text{-Dinitrophenyl n-tri-}$, m.p. 101.5° , *-hepta-*, m.p. 106.5° , and *-octa-decyl sulphone*, m.p. 107.5° . *Di-n-do-*, m.p. $33.5\text{--}34^\circ$, *-tri-*, m.p. $43.5\text{--}44^\circ$, *-tetra-*, m.p. $45.5\text{--}46^\circ$, *-hexa-*, *-hepta-*, m.p. $59.5\text{--}60^\circ$, *-octa-*, and *-nona-decyl disulphide*, m.p. $68.5\text{--}69^\circ$. R. S. C.

Thiocyano-sulphides and -sulphones. A. E. KRETOV and E. M. TOROPOVA (J. Gen. Chem. Russ., 1937, 7, 2009—2015).— $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{S}\cdot\text{Et}$ (I) in AcOH

and H_2O_2 at 100° yield *Et* β -chloroethyl sulphone, b.p. $120\text{--}122^\circ/3\text{--}4$ mm. (I) in EtOH and KCNS (6 hr. at 70°) give *Et* β -thiocyanoethyl sulphide, b.p. $105\text{--}110^\circ/5$ mm., oxidised as above to *Et* β -thiocyanoethyl sulphone, m.p. $36\text{--}37^\circ$. The following compounds are prepared analogously: *Ph* β -chloroethyl, m.p. 52° , *Et*, b.p. $160\text{--}163^\circ/7$ mm., and *Ph* γ -chloropropyl sulphone, m.p. $23\text{--}24^\circ$; *Ph* β -thiocyanoethyl, b.p. $143\text{--}146^\circ/2$ mm., *Et*, b.p. $115\text{--}120^\circ/10$ mm., and *Ph* γ -thiocyanopropyl sulphide, b.p. $176\text{--}178^\circ/3$ mm.; *Ph* β -thiocyanoethyl, m.p. $71\cdot5\text{--}72^\circ$, *Et*, m.p. $39\cdot5\text{--}41^\circ$, and *Ph* γ -thiocyanopropyl sulphone, m.p. 91° .

R. T.

Preparation of esters in presence of aluminium chloride or ferric chloride. A. N. AKOPIAN (J. Gen. Chem. Russ., 1937, 7, 1687—1689).—Esters are obtained in high yield by adding the acid to a solution of AlCl_3 or FeCl_3 in the alcohol, and boiling the mixture under reflux.

R. T.

Hydrolysis of esters by hydrogen chloride with aluminium chloride at catalyst. E. OTT (Ber., 1937, 70, [B], 2362).—Tetraethylsuccinic esters are indifferent towards boiling KOH—EtOH and are unchanged by HCl at 200° . Addition of AlCl_3 to ester and HCl at 200° causes vigorous disengagement of H_2O and alkyl chloride, giving pure tetraethylsuccinic anhydride, b.p. 270° .

H. W.

Reaction of *tert*-butyl chloride with formic acid: *tert*-butyl formate. W. TAYLOR (J.C.S., 1937, 1852—1853).—The conclusion of Bateman and Hughes (A., 1937, I, 467) that hydrolysis of $\text{Bu}^\gamma\text{Cl}$ by H_2O in HCO_2H is unimol. is criticised. $\text{Bu}^\gamma\text{Cl}$, HCO_2H , and $(\text{HCO}_2)_2\text{Ca}$ at room temp. yield *Bu* ^{γ} formate, b.p. $82\cdot5\text{--}83\cdot5^\circ/757$ mm., which is rapidly hydrolysed by $0\cdot1\text{N}$ -NaOH or by N -HCl. The primary reaction may thus be bimol., $\text{Bu}^\gamma\text{Cl} + \text{HCO}_2\text{H} \rightleftharpoons \text{HCO}_2\text{Bu}^\gamma + \text{HCl}$, independent of small $[\text{H}_2\text{O}]$.

E. W. W.

Electrolysis of mixtures of salts of fatty acids with halides and nitrates. F. FICHTER and R. RUEGG (Helv. Chim. Acta, 1937, 20, 1578—1590; cf. A., 1937, II, 84).—Electrolysis of EtCO_2H and HCl with a Pt anode yields β - and α -chloropropionic acid, but no chlorinated hydrocarbon. Butyrate-chloride mixtures give chlorinated acids and their Pr^β esters, C_6H_{14} , and CHCl_3 . *n*-Hexoate + KCl (or KBr) gives *n*- $\text{C}_{10}\text{H}_{22}$ with smaller amounts of *n*-amyl hexoate, Δ^a -pentene, $\text{CH}_2\text{Bu}^a\text{OH}$, CHMePr^aOH , CHEt_2OH , and CHCl_3 (or CHBr_3). Hexoate and nitrate give *n*- $\text{C}_{10}\text{H}_{22}$, *n*- $\text{C}_5\text{H}_{11}\text{NO}_3$, $\text{C}_{10}\text{H}_{21}\text{NO}_3$, and $\text{C}_5\text{H}_{10}(\text{NO}_3)_2$. The nitrates are considered to be formed by the interaction of an ethylene hydrocarbon with anodically activated HNO_3 (cf. A., 1937, II, 45).

F. L. U.

Addition of hydrogen chloride to pentenoic acids. E. SCHJÄNBERG (Ber., 1937, 70, [B], 2385—2391).—The course of addition of HCl to the three pentenoic acids is not influenced by the solvent (heptane, Et_2O , PhMe, EtBr, COMe_2 , BuCl, CHCl_3); in the Δ^a - (I) and Δ^β - (II) -acids Cl occupies the position most distant from $\cdot\text{CO}_2\text{H}$, but the least distant position in the Δ^γ -acid (III). Peroxides do not affect the direction of the addition of HCl

to (III), γ -chlorovaleric acid resulting under all conditions. Increase of pressure and rise of temp. increase the yield of Cl-substituted acids, whereas substances such as Bz_2O_2 , quinol, and FeCl_3 are to be regarded as negative catalysts. Addition is best effected in H_2O , (I) giving a 100% yield exclusively of β -chlorovaleric acid in 2—3 days, whereas (II) and (III) give γ -chlorovaleric acid in 100% yield in 8 days. The behaviour of HCl differs therefore from that of HBr, which depends on solvent and is subject to a peroxide effect.

H. W.

Olefinic acids. XVII. Addition of hydrogen bromide to heptenoic and nonenoic acids with terminal double linkings. P. GAUBERT, R. P. LINSTEAD, and H. N. RYDON (J.C.S., 1937, 1974—1979; cf. A., 1935, 195).—Orientation of addition of HBr to Δ^a -*n*-heptenoic acid (I), Δ^a -*n*-nonenoic acid (II), and $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{H}$ (III) is in agreement with earlier results for the series $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{H}$, i.e., when $n = 1, 2, 3, 4$, or 6 terminal addition occurs in presence of O_2 or peroxides and non-terminal addition in presence of H_2 or antioxidants, whilst in C_6H_{14} anomalous terminal addition occurs even in presence of H_2 or antioxidants. This does not support the view that solvents affect orientation only in so far as they influence the O_2 or peroxide effect. Discrepancy of results in C_6H_{14} with undecenoic acid ($n = 8$) and (III) in results of Kharasch and McNab (A., 1936, 53), who obtained $\text{CHMeBr}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{H}$, is probably due to difference in technique, purity, or capacity of acids to form catalysts. $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ with HBr in absence of solvents or in Et_2O or AcOH yields $\text{CHMeBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, also produced in the presence of peroxides, but in C_6H_{14} , $\text{Br}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ is always produced. This disposes of the contention of Smith (A., 1937, II, 438) that peroxides always reverse the usual orientation.

Constitution of the Br-acids from (I) and (II) is confirmed by synthesis or by conversion into the corresponding dibasic acids by malonation and hydrolysis. Thus ζ -bromo-*n*-heptonic acid (IV), new m.p. 29° , obtained from (I) is synthesised from $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_3\cdot\text{CH}_2\text{Br}$ by conversion into ϵ -phenoxy-*n*-amyl bromide, b.p. $160\text{--}165^\circ/11$ mm., which by malonation gives $\text{OPh}\cdot[\text{CH}_2]_5\cdot\text{CH}(\text{CO}_2\text{Et})_2$, decarboxylated to ζ -phenoxy-*n*-heptonic acid, new m.p. 55° , whence (IV) by action of HBr. β -Methylsuberic acid (V), m.p. 83° , obtained by malonation of (I), is synthesised from Et δ -acetyl-*n*-valerate by condensation with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ to give a product yielding Et β -methyl- Δ^a -*n*-hexene- $\alpha\zeta$ -dicarboxylate, b.p. $160\text{--}162^\circ/10$ mm., whence the Et ester of (V) by distillation. Condensation of Et ϵ -bromo-*n*-hexoate with $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ yields γ -ketononoic acid, b.p. $148^\circ/0\cdot8$ mm., new m.p. 40° , from which β -methylsebacic acid, m.p. $75\text{--}76^\circ$, obtained by malonation of (II), could not be synthesised by a similar process to (V). θ -Bromo-*n*-nonoic acid, from (II) and HBr, has m.p. $37\text{--}38^\circ$.

E. G. B.

Olefinic acids. XVI. Synthesis of Δ^{10} -*n*-undecenoic acid. P. GAUBERT, R. P. LINSTEAD, and H. N. RYDON (J.C.S., 1937, 1971—1974).— Δ^a -*n*-Pentenol (I), prepared by action of Na on tetrahydro-

furfuryl chloride, is brominated by PBr_3 in $\text{C}_5\text{H}_5\text{N}$ to the corresponding bromide, which with $\text{CHNa}(\text{CO}_2\text{Et})_2$ gives $\text{Et}\Delta^8\text{-}n\text{-pentenylmalonate}$, hydrolysed to the corresponding acid (II), m.p. 87° . (II) is decarboxylated to $\Delta^8\text{-}n\text{-heptenoic acid}$ (III), b.p. $125^\circ/15\text{ mm.}$, m.p. -6.5° (*p-toluidide*, m.p. 59.6°). $\text{Et}\Delta^8\text{-}n\text{-heptenoate}$ [from (III) with SOCl_2 and then EtOH] with Na in EtOH gives $\Delta^8\text{-}n\text{-heptenol}$ (IV), b.p. $105^\circ/20\text{ mm.}$ Under the same treatment as (I), (IV) yields successively $\Delta^8\text{-}n\text{-heptenyl bromide}$, b.p. $77\text{--}81^\circ/20\text{ mm.}$, $\Delta^8\text{-}n\text{-heptenylmalonic acid}$, m.p. $90\text{--}91^\circ$, and $\Delta^7\text{-}n\text{-nonenoic acid}$ (V), b.p. $116\text{--}118^\circ/1\text{ mm.}$, m.p. 5° (*p-toluidide*, m.p. 68°). Under the same treatment as (III), (V) yields successively $\Delta^0\text{-}n\text{-nonenol}$, b.p. $135^\circ/20\text{ mm.}$, $\Delta^0\text{-}n\text{-nonenyl bromide}$, b.p. $110\text{--}115^\circ/15\text{ mm.}$, $\Delta^0\text{-}n\text{-nonenylmalonic acid}$, m.p. 107° , and $\Delta^1\text{-}n\text{-undecenoic acid}$, b.p. $131^\circ/1\text{ mm.}$, m.p. $24\text{--}24.5^\circ$, identical with the product obtained from castor oil. The constitution of (III) and (V) is proved by their oxidation by KMnO_4 in NaHCO_3 solution, respectively, to adipic and suberic acids. In KOH solution (V) gives a mixture of pimelic and suberic acids. E. G. B.

Fractional distillation of the fatty acids of phosphatides. W. DIEMER and W. SCHMIDT (*Biochem. Z.*, 1937, 294, 348—352).—Apparatus for the fractional distillation (separation and determination) in a high vac. of 30—5 and $<5\text{ g.}$ of mixed Me esters of the fatty acids ($\text{C}_{15}\text{--}\text{C}_{20}$) is described.

W. McC.

Position of the unsaturated linking in the hexadecenoic acid of certain natural fats. J. M. SPADOLA and R. W. RIEMENSCHNEIDER (*J. Biol. Chem.*, 1937, 121, 787—790).—The Me ester of hexadecenoic acid (I) from goat milk, white rat, and egg-yolk fats (cf. A., 1936, 510) is ozonised and hydrolysed, giving azelaic and *n*-heptic acid; (I) is thus chiefly $\Delta^0\text{-hexadecenoic acid}$.

E. W. W.

Fat of seeds of *Trichosanthes cucumeroides*.—See A., III, 160.

Synthesis of elastic, factice-like substances from fatty acids. See B., 1938, 196.

Course of hydrogenation in mixtures of mixed glycerides. W. J. BUSHELL and T. P. HILDITCH (*J.C.S.*, 1937, 1767—1774).—By partial hydrogenation (Ni-kieselguhr at 180°) of 1:1 binary mixtures of oleodi-palmitin and -stearin, dioleo-palmitin and -stearin, and triolein and determination of the amount of tristearin in the product it is proved that all unsaturated components of a glyceride mixture are reduced concurrently, but that the less saturated components are reduced more rapidly until uniform unsaturation is attained, whereafter the rate of reduction of both components becomes approx. the same. The reported difference in rate of hydrogenation of α - and β -oleyl radicals is disproved. Palmito-oleins are possibly slightly more readily reduced than stearo-oleins. When 3:1 mixtures of α -oleodipalmitin or α -palmitodiolein with triolein are half-reduced, no tristearin is formed. This effect of the relative amounts of the components present accounts for the results obtained with natural fats, which contain 75—80% of palmito-olein. R. S. C.

G** (A., II.)

Autoxidation of unsaturated fatty acids. III. W. FRANKE and D. TERGHEI (*Annalen*, 1937, 533, 46—71; cf. A., 1933, 49).—The rate of absorption of O_2 and the amount absorbed are the same for oleic (I) and ricinoleic (II) acid in bulk and on filter-paper. Both the rate and the amount are, however, larger for linoleic (III) and linolenic acid (IV) on filter-paper. For (I) and (II) in MeOH in presence of 1% of $\text{Co}(\text{NO}_3)_3$ the ratio of peroxide content to O_2 absorbed decreases rapidly with increasing absorption; the I val. \propto absorption up to about 25% absorption, but then decreases more slowly. For (III) and (IV) with various accelerators the peroxide content is theoretical up to about 25% absorption and thereafter increasingly less than theoretical; the I val. falls proportionately up to 60% absorption and thereafter more slowly. The peroxides are fairly stable in MeOH ; the I val. remains const. The results support the view that peroxides are first formed and then decompose to α -OH-ketones; hydrogenation of the acids oxidised to various stages also supports this view. The individual ethylenic linkings of poly-unsaturated acids autoxidise at different rates and the resultant peroxides have different stabilities. R. S. C.

Acylation of ethyl acetoacetate in presence of magnesium. A. SPASSOV (*Ber.*, 1937, 70, [B], 2381—2385; cf. A., 1937, II, 439).—Interaction between $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, acyl chlorides, and Mg occurs readily in C_6H_6 at $80\text{--}85^\circ$, giving *C*-acyl derivatives in yields closely similar to those obtained from $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$. H_2 and HCl are evolved and the change is considered to depend on the direct action of the acid chloride on $\text{OH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, in which Mg or the Mg compound functions as a condensing catalyst. In its acidic character the change differs from the Claisen reaction. Interaction between $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and AcCl , EtCOCl , Pr^cCOCl , Pr^bCOCl , isovaleryl chloride, and BzCl are described. *Et n-butyrylacetoacetate*, b.p. $109\text{--}111^\circ/11\text{ mm.}$ (*Cu* derivative, two forms m.p. $62\text{--}63^\circ$ and $52\text{--}53^\circ$, respectively), and *Et isobutyrylacetoacetate*, b.p. $109.5\text{--}111^\circ/13\text{ mm.}$ (*Cu* compound, m.p. $95\text{--}96^\circ$), appear new. Owing to secondary action of the evolved HCl on $\text{CHAcBz}\cdot\text{CO}_2\text{Et}$, the products derived from BzCl include $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$, $\text{CHAc}_2\cdot\text{CO}_2\text{Et}$, and $\text{CHAcBz}\cdot\text{CO}_2\text{Et}$. H. W.

Labile nature of the halogen atom in organic compounds. XV. Action of hydrazine on bromomalonate esters. H. P. GALLUS and A. K. MACBETH (*J.C.S.*, 1937, 1810—1812).—The rate of reaction of $\text{CBr}_2(\text{CO}_2\text{R})_2$ or $\text{CHBr}(\text{CO}_2\text{R})_2$ with N_2H_4 , and the vol. of N_2 evolved, decrease as the size of R increases (cf. *J.C.S.*, 1922, 121, 904). That this may in part be due to replacement of Br by OH instead of H is suggested by the isolation of *mesoxal-hydrazide hydrazone*, m.p. 187° , after reaction of N_2H_4 with *Bu* $^\beta$, b.p. $138^\circ/10\text{ mm.}$, or *isoamyl dibromomalonate*, b.p. $142\text{--}143^\circ/4\text{ mm.}$ *Bu bromo-*, b.p. $135\text{--}136^\circ/10\text{ mm.}$, and *dibromo-malonate*, b.p. $147^\circ/10\text{ mm.}$, *Bu* $^\beta$, b.p. $124\text{--}126^\circ/12\text{ mm.}$, *n-amyl*, b.p. $144^\circ/4\text{ mm.}$, *isoamyl*, b.p. $146\text{--}148^\circ/11\text{ mm.}$, *sec-octyl*, b.p. $169\text{--}170^\circ/4\text{ mm.}$, and *cyclohexyl bromomalonate*, b.p. $167^\circ/4\text{ mm.}$, are prepared, and 2-, b.p. $176^\circ/6\text{ mm.}$, 3-, b.p. $182^\circ/6\text{ mm.}$, and 4-methyl-

cyclohexyl bromomalonate, b.p. 180—181°/4 mm., are obtained slightly impure. The reactions of these, and of simpler bromo- and dibromomalonates, with N_2H_4 are studied. *n-Octyl*, b.p. 176—177°/6 mm., cyclohexyl, b.p. 173°/10 mm., and 2-, b.p. 172—173°/10 mm., 3-, b.p. 178°/13 mm., and 4-methylcyclohexyl malonate, b.p. 168°/10 mm., are described.

E. W. W.

Autoxidation of maleic anhydride- β -elæostearin.—See A., I, 37.

Ethyl acetonedicarboxylate. I. G. JACINI (Gazzetta, 1937, 67, 715—719).—

$(CH_2 \cdot CO_2Et)_2C \cdot N \cdot NH \cdot CO \cdot NH_2$ (I) is hydrolysed by boiling H_2O , giving $(NH \cdot CO \cdot NH_2)_2$, and in 20% aq. NH_3 at room temp. yields the NH_4 salt, m.p. 144°, of 2:6-dihydroxy-4-pyridone semicarbazone, m.p. 165—167°. When fused and heated at 100—105°, (I) loses $EtOH$, forming a substance, $C_8H_{11}O_4N_3$, m.p. 129°; at 120° a product, m.p. >350°, is formed. These reactions are compared with those of $CO_2Et \cdot CH_2 \cdot CMe \cdot N \cdot NH \cdot CO \cdot NH_2$.

E. W. W.

Reaction of tartaric acid: Pesez' reaction. C. H. LIBERALLI (Rev. Quim. Farm., 1935, 1, 23—24; Chem. Zentr., 1936, i, 4473).—Pesez' method is preferable to the Möhler-Denigès test. Iodides may be removed with HNO_3 , but vanadates interfere.

J. S. A.

Action of diazomethane on saccharic acid. O. T. SCHMIDT, H. ZEISER, and H. DIPPOLD (Ber., 1937, 70, [B], 2402—2415).—Saccharic acid (I), like tartaric and trihydroxyglutaric acid, is extensively methylated at the free OH groups, but the production of a double linking appears unique. The action of CH_2N_2 , whether obtained from nitrosomethyl-ureth-

ation of (II) gives an aldehyde-ester (not isolated) hydrolysed to $H_2C_2O_4$ in theoretical yield with a simply methylated tetrauronic acid oxidised by Br to *d*-hydroxymethoxysuccinic acid, m.p. 179°, $[\alpha]_D^{20} +49.6^\circ \pm 0.6^\circ$ in H_2O . The further elucidation of the constitution of (II) rests on the application of Hudson's lactone rule. Unexpectedly the yield of (II) obtained from saccharolactonic acid (IV) and CH_2N_2 is > that obtained from the acid; possibly a revision of the structure of (IV) is necessary. Detailed description is given of the non-cryst. products obtained during the methylation of (I); they are more highly methylated and, in part, unsaturated.

H. W.

Pectin substances. I. Sugar-beet pectins. T. K. GAPONENKOV (J. Gen. Chem. Russ., 1937, 7, 1986—1991).—Sugar-beet protopectin, hydratopectin, araban, pectic acid, and galacturonic acid have been prepared, and certain consts. are recorded for the preps.

R. T.

Photochemical decomposition of aliphatic aldehydes in aqueous solutions.—See A., I, 39.

Kinetics of polymeric aldehydes. IX. Gross constants of the dissolution process of solid polyoxymethylenes. K. P. JUNG and J. LÖBERING (Ber., 1937, 70, [B], 2415—2427; cf. A., 1938, II, 4).—The rate of dissolution of solid polyoxymethylenes (I) is either \propto the actual amount of suspended material or is const. over a portion of its total course. The character of the process is determined by the magnitude of the solubility product of the suspended (I) in relationship to the consts. of the contributing reactions.

H. W.

Synthesis of Δ^8 -octadienal. G. GOETHALS (Bull. Soc. chim. Belg., 1937, 46, 409—422).—Me Δ^8 -pentenoate reduced (Na-MeOH) yields *n*- $C_5H_{11} \cdot OH$ and Δ^7 -pentenol, which with $SOCl_2$ and C_5H_5N in CH_2Cl_2 yields Δ^7 -pentenyl chloride (I), b.p. 107—107.5°/755 mm., converted (NaI in $COMe_3$) into Δ^7 -pentenyl iodide (II), b.p. 53.6°/20 mm. The Grignard compound, prepared from a mixture of (I) and (II), is converted by acraldehyde into pentenylvinylcarbinol, b.p. 72.5—75.5°/10 mm., which is brominated (PBr_3 and C_5H_5N) in light petroleum to octadienyl bromide, b.p. 72—75°/10.5 mm. This, when heated with $AgOBz$ in abs. Et_2O , yields octadienyl benzoate, b.p. 122—131°/0.8 mm., hydrolysed (KOH-MeOH) to Δ^8 -octadienol, b.p. 88—90.5°/10 mm., oxidised ($K_2Cr_2O_7-H_2SO_4$) to Δ^8 -octadienal, b.p. 77—79°/10 mm. (semicarbazone, m.p. 169.3—170°).

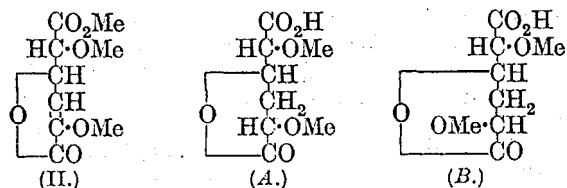
J. D. R.

Products formed during the preparation of keten. R. W. HALE (Nature, 1937, 140, 1017).—Traces of $C_{10}H_8$ have been detected in the $COMe_2$ condensate obtained during the prep. of keten by passing $COMe_2$ over electrolytic Cu heated in a SiO_2 tube.

L. S. T.

Photo-oxidation of acetone vapour.—See A., I, 39.

Ketals of hydroxyketones. II. Acetoin ketal. V. V. EVLAMPIEV (J. Gen. Chem. Russ., 1937, 7, 1579—1580).— $COMe \cdot CHMe \cdot OAc$, $CH(OEt)_3$, and $p-C_6H_4Me \cdot SO_3H$ yield the ketal, b.p. 88.5—90°/14



ane or -carbamide, on (I) gives a 26% yield of the unsaturated lactone ester (II), m.p. 87°, $[\alpha]_D^{20} +83.1^\circ \pm 0.6^\circ$ in abs. MeOH, which immediately reduces alkaline $KMnO_4$, gives a faint but distinct colour with $C(NO_2)_4$ in $EtOH$, slowly adds 1 H_2 and 2 Br, but does not give a colour with $FeCl_3$. Hence the double linking lies between C atoms to which OH is not attached. The lactone is opened with greater difficulty than is customary with γ -lactones of the sugar group. Hydrolysis of (II) gives the corresponding unsaturated lactone acid (III), m.p. 168°, $[\alpha]_D^{20} +72.5^\circ \pm 0.5^\circ$ in H_2O , in which the relative stability of the lactone ring is pronounced. Hydrogenation of (III) gives the saturated lactone acid, m.p. 128—129°, $[\alpha]_D^{20} +98.4^\circ \pm 0.4^\circ$ in H_2O (corresponding free dicarboxylic acid, $[\alpha]_D^{20} -21.6^\circ \pm 0.8^\circ$ in H_2O , and its Na_2 salt, $[\alpha]_D^{20} -21.2^\circ \pm 0.4^\circ$ in H_2O), which appears to be one of the homogeneous forms A or B. Hydrogenation of (II) gives a syrup apparently hydrolysed to a mixture of A and B, from which a saturated acid, m.p. 144—145°, $[\alpha]_D^{20} +84.7^\circ \pm 0.4^\circ$ in H_2O (initial), is isolated. Ozonis-

mm., of acetoin acetate, converted by heating at 80° with aq. $\text{Ca}(\text{OH})_2$ into *acetoin ketal*, b.p. 82.5°/23 mm.

R. T.

Configuration of carbohydrates from conductivity measurements in boric acid solution. H. T. MACPHERSON and E. G. V. PERCIVAL (J.C.S., 1937, 1920—1927).—Conductivity measurements in H_3BO_3 solution with α -methylglucopyranoside, 2:3:6-tri- and 2:3:4:6-tetra-methyl-glucopyranosides and -methylglucopyranosides, and sucrose show that the ring O has no effect on conductivity of H_3BO_3 , and that, in the case of glucose, the only OH groups with a positive effect are those at $\text{C}_{(1)}$ and $\text{C}_{(2)}$, thus confirming Böeseken's configuration (A., 1913, i, 1147) for α - and β -glucose. Depressions of conductivity are shown to be not anomalous by relative viscosities, which run parallel. Initial elevation of conductivity shown by β -glucose may be due to the presence of small amounts of the straight-chain aldehydic form. Contrary to Böeseken and Couvert (A., 1921, i, 497), β -*D*-mannose shows a fall in conductivity during mutarotation in keeping with its accepted *cis*-configuration and confirmed by the initial depression, decreasing during mutarotation, given by 3:4:6-trimethyl- α -*D*-mannose. α -*L*-Rhamnose shows a rise of conductivity during mutarotation in agreement with *trans*-configuration. The high elevation shown by α -methylmannofuranoside is attributed to proximity of the $\text{C}_{(2)}$ and $\text{C}_{(3)}$ OH-groups to the side-chain $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$; γ -methylglucoside, with three OH in proximity, gives a lower elevation, and γ -methylgalactoside a depression. The group $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ alone has no effect on conductivity, since it is capable of free rotation. α -*L*-Sorbitol gives an anomalous high elevation.

Results for OH-compounds in general show no considerable rise in conductivity until four OH are present. H_3BO_3 may react with H_2O in solution to give $\text{H}[\text{B}(\text{OH})_4]$, the OH of which may be associated with the H of the org. OH-residue by OH-linkings. Increase in the no. of these decreases the negative charge on the B; thus increasing the tendency to loss of H^+ . The *cis*-OH at $\text{C}_{(3)}$ and $\text{C}_{(4)}$ in pyranoses have no positive effect on conductivity. *cis*-cyclopentane-1:2-diol gives an increase and *cis*-cyclohexane-1:2-diol a decrease of conductivity, probably due to the OH being adjacent in the flat five-C ring and not in the strainless six-C ring.

E. G. B.

Mechanism of formation of sugars from formaldehyde. S. A. BALEZIN (J. Gen. Chem. Russ., 1937, 7, 2099—2115).—Condensation of CH_2O in presence of aq. $\text{Ca}(\text{OH})_2$ at 40—45° gives chiefly aldohexoses; in addition HCO_2H , MeOH, and pentoses are formed. The yield of sugars is greater when glucose is present initially. The reaction is conveniently followed dilatometrically; dissolution of the substrates is followed by a rapid fall in vol., followed by a gradual rise, attaining a max. after 105 min. at 45°; and after 3 hr. at 40°, and followed by a second fall in vol., lasting 7—10 min. Formation of sugars takes place during this period, and proceeds to completion only when 6 mols. of CH_2O are present per Ca^{++} . The induction period is greatly shortened

by addition of glucose or fructose, but not sucrose. Further incubation after completion of the period of sugar formation leads to decomp. of sugars, causing a further increase in vol. The apparent mol. wt.-time curves have the same shape as the dilatometer curves, whence it is concluded that an intermediate product of higher mol. wt. than hexose is being formed during the induction period, and decomposes to yield hexose in the succeeding period.

R. T.

Microanalysis of carbohydrates in vegetable substances.—See A., III, 159.

New preparation of osones. R. WEIDENHAGEN (Z. Wirts. Zuckerind., 1937, 87, 711—715).—Oxidation of sugars occurs almost homogeneously and leads mainly to osones when a moderate excess of $\text{Cu}(\text{OAc})_2$ is used for a short time in EtOH or, preferably, in conc. MeOH. *L*-Sorbitol and *L*-xylose (I) are thus obtained in at least 60% yield by direct oxidation of the respective sugars. The solutions of (I) have the further advantage that they can be used directly without further purification or isolation of the osone for the addition of HCN in the synthesis of vitamin-C (II). This takes place almost quantitatively, and the further operations can be so conducted that (II) is obtained in 42% yield calc. on the dissolved (I). Of this 50% crystallises directly on concn., and further amounts can be obtained from the mother-liquors. The solid material is of 95% purity. *D*-Xylosone is obtained in 60% yield from *D*-xylose. In contrast with sorbitol, the yields with the other hexoses attain only 40%; this is reached by galactose, which under other conditions does not yield any osone.

H. W.

Conversion of uronic acids into corresponding hexoses. II. Catalytic reduction of the methyl ester of 2:3:4-trimethyl- α -methyl-*D*-galacturonide. P. A. LEVENE, R. S. TRIPSON, and L. C. KREIDER. III. Catalytic reduction and deacetylation of the methyl ester of α -methyl-*D*-galacturonide 2:3:4-triacetate. P. A. LEVENE and C. C. CHRISTMAN (J. Biol. Chem., 1937, 122, 199—202, 203—205; cf. A., 1937, II, 484).—II. The Me ester, $[\alpha]_D^{25} +166.1^\circ$ in H_2O , $+155.9^\circ$ in abs. MeOH, $+142.7^\circ$ in CHCl_3 , $+149.3^\circ$ in COMe_2 , $+166.5^\circ$ (const.) in N-HCl , of 2:3:4-trimethyl- α -methyl-*D*-galacturonide with H_2 and Cu chromite in MeOH at 175°/4300 lb. gives a good yield of 2:3:4-trimethyl- α -methyl-*D*-galactoside, m.p. about 30°, b.p. about 140° (bath)/0.3 mm., $[\alpha]_D^{25} +198.4^\circ$ in H_2O , $[\alpha]_D^{25} +160.8^\circ$ in abs. MeOH, hydrolysed by N-HCl to 2:3:4-trimethyl-*D*-galactose, m.p. 82—83°, $[\alpha]_D^{25} +156^\circ \rightarrow 119.1^\circ$ in H_2O in 90 min.

III. Hydrogenation (Cu chromite) of the Me ester of α -methyl-*D*-galacturonide reduces some of the OH, but that of the triacetate of this ester at 175°/3000—4300 lb. in MeOH gives α -methyl-*D*-galactoside. The Me ester of α -methylaldobionide hexa-acetate is probably similarly reduced and deacetylated. Glucosides of uronic acids give no ppt. with boiling $\text{Ba}(\text{OH})_2$ solutions.

R. S. C.

1:5-Anhydride of 2:3:4:6-tetramethyl-glucose-1:2-enediol [2:3:4:6-tetramethyloxy-glucal]. M. L. WOLFRAM and D. R. HUSTED (J.

Amer. Chem. Soc., 1937, **59**, 2559—2561).—1-Bromo-2:3:4:6-tetramethyl-*D*-glucose (prep. from the acetate and HBr in Ac_2O - AcOH at 0°) with NHET_2 in C_6H_6 gives 1-diethylamino-2:3:4:6-tetramethyl-*D*-glucose, b.p. $62\text{--}65^\circ/10^{-4}$ mm., m.p. 34° , $[\alpha]_D^{25} -2.8^\circ$ in MeOH, $[\alpha]_D^{25}$ about -8° in saturated aq. H_3BO_3 changing to $+64.8^\circ$ by hydrolysis of the NET_2 (reduces Fehling's solution only after hydrolysis). With NaOH in dry dioxan- Et_2O it gives 2:3:4:6-tetramethyl-1:2-*D*-glucoseen [-oxyglucal], b.p. $50\text{--}55^\circ/10^{-3}$ mm., $99.2\text{--}99.5^\circ/4$ mm., m.p. 12° , $[\alpha]_D^{30} +15^\circ$ in H_2O , $+4^\circ$ in CHCl_3 , which reduces Fehling's solution only after hydrolysis or when kept, absorbs 2 I under Wijs' conditions, and absorbs 4 I from NaIO_3 .

R. S. C.

Glycofuranosides and thioglycofuranosides.
II. Crystalline α -ethylgalactofuranosides. J. W. GREEN and E. PACSU (J. Amer. Chem. Soc., 1937, **59**, 2569—2570).—2% of α -ethylgalactofuranoside, m.p. $139\text{--}140^\circ$, is obtained from the mother-liquors from the β -isomeride (A., 1937, II, 369). The structure follows from the difference of its $[\alpha]_D^{20}$ ($+92^\circ$ in H_2O) from that of the β -compound and from the rate of hydrolysis ($k = 0.08$) by 0.05N -HCl. R. S. C.

Tagatose and methyltagatose. (MME.) Y. KHOUVINE and Y. TOMODA (Compt. rend., 1937, **205**, 736—738).— α -*D*-Tagatose (I), m.p. 162° (block), $[\alpha]_D^{20} -3.9^\circ$ in H_2O , shows mutarotation which is not due to the presence of galactose. (I) in MeOH at 28° with dry HCl affords methyltagatose, m.p. 128° (block), $[\alpha]_D^{20} +56.8^\circ$ in MeOH, which has no reducing properties and is hydrolysed by acid, but not by emulsin, to (I). (I) with boiling MeOH containing HCl gives mixtures of substances. J. L. D.

Structure of two sorbose penta-acetates. G. ARRAGON (Compt. rend., 1937, **205**, 735—736).—Sorbose tetra-acetate with Ac_2O containing H_2SO_4 at -5° affords a sorbose penta-acetate (I), m.p. 95° , $[\alpha]_D^{20} -52.4^\circ$ in CHCl_3 ; with Ac_2O - ZnCl_2 a sorbose penta-acetate (II), identical with that described previously (cf. A., 1933, 811), is formed. Hydrolysis of (I) and (II) affords sorbose (III); methylation of (I), (II), and (III) gives the same methylsorbose. (II) but not (I) shows a strong absorption band at 2700 A. which is characteristic of C=O. (II) with H_2 -Raney Ni in MeOH affords, after acetylation, *D*-iditol hexa-acetate; (I) does not react similarly, indicating that it probably has a pyranose structure. J. L. D.

Synthesis of aldobionides. W. F. GOEBEL, R. E. REEVES, and R. D. HOTCHKISS (J. Amer. Chem. Soc., 1937, **59**, 2745).—The Me ester hepta-acetate of cellobiuronic acid or of the acacia aldobionic acid with HBr- AcOH gives the Me ester hexa-acetate, m.p. 200° , $[\alpha]_D^{25} +99.4^\circ$ in CHCl_3 , and m.p. $201\text{--}202^\circ$, $[\alpha]_D^{25} +194.7^\circ$, of α -bromo-4- β -glucuronisidoglucose and 6- β -glucuronisidoglucose, respectively. The latter with MeOH- Ag_2O gives 6- β -glucuronisidomethylgalactoside Me ester hexa-acetate, m.p. 134° , $[\alpha]_D^{25} +86.4^\circ$, which is probably an α - and not, as expected, a β -glucoside. R. S. C.

Mol. wt. of araban. T. K. GAPONENKOV (J. Gen. Chem. Russ., 1937, **7**, 1729—1732).—The mean mol. wt. as determined by the osmotic pressure,

cryoscopic, terminal group, and viscosity methods is 6328, 2522, 4970, and 1102. The terminal group method is the most trustworthy; the high results given by the osmotic pressure method are ascribed to presence of low mol. wt. fragments in the sample, and the low results given by the other two methods are due to hydration of the araban mols., and to the non-applicability to araban of the Staudinger η coeff. for cellulose. R. T.

Polysaccharides. XXVI. Xylan. R. A. S. BYWATER, W. N. HAWORTH, E. L. HIRST, and S. PEAT (J.C.S., 1937, 1983—1988; cf. A., 1937, II, 277).—Earlier work has shown that xylan (I) consists of linked chains of xylopyranose units terminated at one end by arabofuranose units. By treatment of (I) with 0.005N - HNO_3 partial removal of arabinose occurs, as shown by methylation and hydrolysis of the product (xylan A) (II) to a mixture of trimethylpentoses consisting of trimethylarabofuranose and trimethylxylopyranose. With 0.2% $\text{H}_2\text{C}_2\text{O}_4$, however, (I) yields as arabinose-free xylan (III) which on methylation and fractionation gives a product (IV), $[\alpha]_D^{21} -91.2^\circ$ in CHCl_3 [methylated (I) has $[\alpha]_D^{20} -98.3^\circ$], with viscosity $<$ and reducing power $>$ that of methylated (I). Hydrolysis of (IV) and fractionation gives a 7% yield of trimethylmethylxylopyranoside, corresponding with a chain length in (I) of 18—19 xylose units, in agreement with earlier work. (I), (II), and (III) have the same chain length. (I) probably consists of primary chains, arabinose-(xylose) $_{16-17}$ -xylose, linked through the free xylose reducing group and an OH (possibly at C_{63} of a xylose residue) in a second chain. This link is relatively stable to alkaline methylating agents and does not involve the arabofuranose unit since this functions as an end group. This linked chain structure is common to most polysaccharides. E. G. B.

Reactions relating to carbohydrates and polysaccharides. LIH. Structure of the dextran synthesised by the action of *Leuconostoc mesenteroides* on sucrose. F. L. FOWLER, I. K. BUCKLAND, F. BRAUNS, and H. HIBBERT (Canad. J. Res., 1937, **15**, B, 486—497).—Dextran (I) (tribenzoate, $[\alpha]_D +193.7^\circ$ in CHCl_3 - CHCl_3 ; triacetate; Me_3 derivative (II), $[\alpha]_D^{21} +202.2^\circ$ in CHCl_3 - CHCl_3) is hydrolysed by dil. H_2SO_4 to glucose. Hydrolysis of (II) with MeOH-HCl gives 2:3-dimethyl-, 2:3:4-trimethyl-, and 2:3:4:6-tetramethyl-methylglucoside in the ratio 1:3:1. (I) is thus probably a polymeride of a pentaglucopyranose anhydride. One of the glucopyranose units is attached as a side-chain, the remaining four being most probably connected by linear linkings. Three of the linkings between glucopyranose units are of the 1:6 type; the remaining two are 1:4 or 1:6. The antigenic properties shown by (I) probably result from the presence of glucose side-chains. D. E. W.

Comparative study of solutions of amylose, amylophosphoric acid, and cellulose.—See A., I, 79.

Plant colloids. XLV. Alkali-lability as a characteristic of starch substances. M. SAMEO (Kolloid-Beih., 1937, **47**, 91—99; cf. A., 1937, II,

370).—Examination of the suitability of "alkali-lability" (alteration of reducing power after treatment with alkali) for characterising different starches and starch products shows a general, but not invariable, parallelism between the reducing power of the original and the "alkali-labile" substance, amounting to a const. ratio in the dextrin group. There is no relation between alkali-lability and I consumption.

F. L. U.

Highly polymerised compounds. CLXXXII. [Lieser's micellary theory of cellulose.] H. STAUDINGER (Ber., 1937, 70, [B], 2514—2517).—In reply to Lieser (A., 1937, II, 179) it is considered that in the present condition of the investigation of cellulose (I) the conception of micelle should be confined to the solid state; the colloidal particles in dil. solutions of (I) and its derivatives are macromols. The cryst. portions of solid (I) are crystallites which have a mol. lattice. Such a crystallite can be regarded as a micelle according to Nägeli's definition.

H. W.

Highly polymerised compounds. CLXXXI. Solutions of cellulose. H. STAUDINGER and G. DAUMILLER (Ber., 1937, 70, [B], 2508—2513).—The vals. of $K_m \times 10^4$ are 4.2, about 5.5, 5.0, 8.0, 8.0, 18—21, and 20, respectively, for cellulose (I) in $\text{NEt}_3\cdot\text{OH}$, NaOH , and LiOH , Schweitzer's reagent, $\text{Cu}(\text{CH}_2\text{NH}_2)_2$ solution, $\text{Ca}(\text{CNS})_2$, H_3PO_4 , and H_2SO_4 at 20° . The differences are much more marked than those observed with homopolar complex compounds in different homopolar media. This is ascribed to the fact that (I) is present as alkoxide in alkali solutions, as oxonium salt in acids, and as Cu complex in solutions of Cu salts. It is further obvious that (I) is present similarly in all these solvents, since the simple relationships between the sp. viscosity of the polymeric-homologous celluloses in different media are inexplicable if the condition is sometimes micellary and at other times mol.

H. W.

Highly polymerised compounds. CLXXX. Degree of polymerisation of cellulose in different varieties of wood. H. STAUDINGER, E. DREHER, and I. JURISCH (Ber., 1937, 70, [B], 2502—2507).—The proportion of cellulose (I) and cellopolyoses (II) [(I) + hemicelluloses] in finely divided poplar, pine, silver fir, spruce, and beech is determined by extraction with EtOH , C_6H_6 , and Et_2O for 15 hr., desiccation at about $50^\circ/\text{vac.}$, and treatment of the residue with Schweitzer's solution in absence of light and air. From this solution (II) are pptd. by Na K tartrate and, after re-pptn., have degree of polymerisation 900—1200, according to the variety of the wood. They are therefore somewhat more complex than sulphite- and soda-cellulose. Treatment of wood with 40% NaOH gives only incomplete rupture of the linkings between (II) and the other constituents of the wood. Treatment of wood with $\text{Ca}(\text{HSO}_3)_2$ or NaOH gives (II) which are sol. in Schweitzer's reagent and have degree of polymerisation 500—1000, mainly dependent on the nature of the bleaching process. Treatment of wood with dil. HNO_3 gives moderately complex (I), but the products obtained by use of HCl in dioxan and, particularly, of H_2O and EtOH at 185° are greatly degraded.

$\text{Cl}_2\text{--H}_2\text{O}$ and other oxidising agents degrade (I), which, however, is little affected by 0.25% ClO_2 . Treatment of wood sawdust with 0.25% ClO_2 and $\text{C}_5\text{H}_5\text{N}$ for 1—2 days causes removal of lignin to such an extent that the residual (II) are more or less completely sol. in Schweitzer's reagent; the process is more rapid with aged than with fresh sawdust. Determinations of the viscosity of (II) obtained in this manner show their degree of polymerisation to be similar to that of the fibre celluloses. H. W.

Flax cellulose. J. DĄBROVSKI and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1937, A, 201—216).—Flax and cotton cellulose behave identically when hydrolysed to glucose by acid, methylated, acetylated, or converted into hydrocellulose (cf. Marchlewski *et al.*, A., 1935, 913). The Ac derivatives of the two celluloses are similar in $[\alpha]$, η , and Cu no., which vary according to the method of prep.; small η is correlated with large Cu no. The Me and Ac derivatives show continuous absorption in the ultra-violet; the hydrocelluloses show slight selective absorption in NaOH , increasing with time of contact. Hydrolysis of both celluloses gives solutions the $[\alpha]$ of which, originally high, decreases until about in accord with the amount of sucrose determined by Bertrand's method. R. S. C.

Beech wood (*Fagus sylvatica*). E. SCHMIDT, W. JANDEBEUR, M. HECKER, E. COFFARI, and E. J. STOETZER [with K. MEINEL] (Ber., 1937, 70, [B], 2345—2360).—The successive action of ClO_2 and $\text{C}_5\text{H}_5\text{N}$ on beech wood transforms the lignin into sol. compounds and leaves the skeleton substance (I), about 77% of the wood, which consists of cellulose (II), xylan acetate, and the freely sol. polymeric carbohydrates. Treatment of (I) with 0.04—0.2% NaOH leaves an insol. product (III) consisting of (II) and deacetylated xylan (IV). (II) is obtained by the action of 5% NaOH containing NaCl on (III). It contains 0.282% CO_2H , in agreement with observation on native cotton cellulose and native *B*-cellulose (from sucrose and *B. xylinum*). It also contains 0.197% OMe , and since 0.199% OMe is equiv. to 0.282% CO_2H , it follows that each chain of (II) contains 96 C_6 individual links. The composition of (III) is invariable and independent of the age and origin of the investigated wood. (III) constitutes about 57% of the wood and contains 78.4% of (II) and 21.6% of (IV) corresponding with the ratio $(\text{C}_6\text{H}_{10}\text{O}_5)_3 : (\text{C}_5\text{H}_8\text{O}_4)_1$. (III) contains 0.661% CO_2H , which corresponds with 2.04% of CO_2H in (IV), which therefore contains 16 C_5 individual links in its chain. In isolated (IV) 1.88% of CO_2H is observed, so that the material is not completely stable towards 5% NaOH , though stable to the 0.2% solution. (III) of every age and from every source contains 0.466% of OMe , which is stable towards NaOH , and hence is in ether-like union. This corresponds with the presence of 1.44% of OMe in (IV), whereas 1.35% is found in the isolated material. 0.466% OMe and 0.661% CO_2H are equimol. The criteria of native composition are observed in (II) and (III) only when the wood is healthy. Wood badly damaged by frost contained >0.282% CO_2H and had the composition $(\text{C}_6\text{H}_{10}\text{O}_5)_{2.86}(\text{C}_5\text{H}_8\text{O}_4)_1$. Xylan, with 2.04% CO_2H ,

appears to be the carrier of the ester-like Ac group of beech wood, and since the integral relationship, xylose anhydride:Ac = 1:1, is established, the expression $(C_6H_{10}O_5)_3(C_5H_7O_4Ac)$ is obtained for (I). This appears characteristic of all cell walls of beech.

H. W.

Highly polymerised compounds. Determination of the viscosity of cellulose nitrates. H. STAUDINGER and M. SORKIN (Ber., 1937, 70, [B], 2518).—A mathematical extension of published work (A., 1937, II, 447).

H. W.

Additive complexes of hydrogen peroxide with organic compounds. J. H. KREPELKA and R. BUKSA (Chem. Listy, 1937, 31, 447—455).—Crystal hydrate H_2O may be replaced by H_2O_2 , by dissolving the substance in H_2O_2 at low temp., and pptg. with $EtOH-Et_2O$. The following complexes are described: $(CH_2)_6N_4 \cdot 1.5H_2O_2$, $CH_3(CO \cdot NH \cdot NH_2)_2 \cdot H_2O_2$, $HCO_2Na \cdot H_2O_2$, $CHMeCl \cdot CO_2Na \cdot H_2O_2$, quinine, $H_2SO_4 \cdot 2.5H_2O_2 \cdot H_2O$, quinine, $2HCl \cdot 1.5H_2O_2 \cdot H_2O$, $NH_2 \cdot CH_2 \cdot CO_2H \cdot 1.5H_2O$. The stability of these compounds varies approx. parallel with their basicity.

R. T.

Methylation of glucosamine. W. O. CUTLER, W. N. HAWORTH, and S. PEAT (J.C.S., 1937, 1979—1983).—Reduction of the activity of NH_2 by substitution is necessary to avoid decomp. of glucosamine (I) during methylation. *CHPh*, m.p. 156° (decomp.), and *o*-hydroxy- and *p*-methoxy-benzylidene derivatives of (I) cannot be methylated in aq. alkaline solution owing to decomp. to (I) and *PhCHO* etc. The penta-acetate (II) of (I) with Me_2SO_4 in NaOH yields *N*-acetyltrimethyl- β -methylglucosaminide (III), m.p. 195° , $[\alpha]_D^{25} +19.6^\circ$ in $CHCl_3$, $[\alpha]_D^{25} -29.0^\circ$ in H_2O , $[\alpha]_D^{25} -13.1^\circ$ in dry MeOH, obtained in better yield from acetobromoglucosamine hydrobromide by conversion into the β -methylglucoside, and acetylation to *N*-acetyltriacetate- β -methylglucosaminide, m.p. 159° , $[\alpha]_D^{25} -21.0^\circ$ in MeOH, followed by methylation. (III) is converted by 5% HCl into trimethylglucosamine hydrochloride, decomp. 210° , $[\alpha]_D^{25} +56.8^\circ$ in MeOH, mutarotating in H_2O , $[\alpha]_D^{25} +49.2^\circ \rightarrow +99.4^\circ$. With 2% HCl in MeOH, (III) yields *N*-acetyltrimethyl- α -methylglucosaminide (IV), m.p. 150° , $[\alpha]_D^{25} +120.0^\circ$ in $CHCl_3$, $[\alpha]_D^{25} +104.3^\circ$ in H_2O , $[\alpha]_D^{25} +135.0^\circ$ in dry MeOH. With boiling 7% HCl in MeOH, (III) and (IV) both give trimethyl- α -methylglucosaminide hydrochloride (V), decomp. 237° , $[\alpha]_D^{25} +129.6^\circ$ in H_2O , $[\alpha]_D^{25} +113.6^\circ$ in MeOH, which with $NaHCO_3$ gives the free amine, $[\alpha]_D^{25} +169.8^\circ$ in dry MeOH, from which (V) is regenerated by boiling with 2% HCl in MeOH. The α -configuration of (V) and (VI) is shown by their acetylation to (IV).

E. G. B.

Action of sodium glycocholate on fatty acids and soaps. I. Dissolving action of glycocholate. K. HOLWERDA (Biochem. Z., 1937, 294, 372—389; cf. Verzár and Kúthy, A., 1929, 1194).—The amount of saturated fatty acid (I) brought into aq. solution (PO_4 buffer) by a fixed amount of Na glycocholate (II) at p_H 6.0—6.2 and 18—20° [octoic acid (III) at 37°] decreases greatly as the C chain of (I) lengthens, the approx. max. no. of mols. of (II) required for dissolving 1 mol. of (I) being: (III) <0.35, decoic <0.75, undecoic <2.2, lauric <2.5,

myristic <7, palmitic <10. The length of the chain directly affects the stability and composition of the association product, increasing length of chain tending to increase this stability and consequently to increase the amount of (I) held in solution. Opposed to this tendency, however, is the more powerful indirect effect of decreasing solubility of (I) in H_2O (or H_2O + buffer) as length of chain increases.

W. McC.

Crystalline anhydrous and monohydrated *dl*-glutamic acid. M. S. DUNN and M. P. STODDARD (J. Biol. Chem., 1937, 121, 521—529).—Na *d*-glutamate and NH_4Cl at 230—235° give a product (containing *dl*-pyroglutamide and *dl*-2-pyrrolidone-carboxylic acid), which with boiling 6*N*-HCl gives *dl*-glutamic acid (I). Crystallographic data are given for the monohydrate of (I), distinguishable microscopically from the anhyd. form; the existence of the two forms may explain previous discrepancies in solubility data (A., 1934, 139).

E. W. W.

Oxidation of cysteine in non-aqueous media. "Sulphenic acid" as primary oxidation product. G. TOENNIES (J. Biol. Chem., 1938, 122, 27—47).— Bu^tOH is the best medium for the demonstration of the "sulphenic acid" among the S-containing products which are pptd. from cysteine perchlorate solutions by the action of $H_2S_2O_8$. The "sulphenic acid" is present in variable amounts.

P. G. M.

Reactions of semimercaptals with amino-compounds. M. P. SCHUBERT (J. Biol. Chem., 1937, 121, 539—548; cf. A., 1936, 824).—The OH of $OH \cdot CH_2 \cdot S \cdot CH_2 \cdot CO \cdot NHPh$ (I) reacts with NH_2 -compounds to form aminomethyl thioethers. With 2:4:1- $(NO_2)_2C_6H_3 \cdot NH \cdot NH_2$ in AcOH, 2:4-dinitrophenylhydrazinomethylthiolacetanilide, m.p. 125—127°, is formed. $NHPh \cdot NH_2$, (I), EtOH, and aq. KOAc yield phenylhydrazinobismethylthiolacetanilide, $NHPh \cdot N(CH_2 \cdot S \cdot CH_2 \cdot CO \cdot NHPh)_2$, m.p. 120—122°. With $C_5H_{11}N$ in EtOH, piperidinomethylthiolacetanilide, m.p. 60—61° (hydrochloride, m.p. 180—182°), is formed, and with glycine, carboxymethylaminobismethylthiolacetanilide, m.p. 109°. *o*- $NH_2 \cdot C_6H_4 \cdot CO_2H$ yields *o*-carboxyphenylaminomethylthiolacetanilide, m.p. 146—148°. These compounds behave as if dissociated in EtOH; thus they react readily with I, and all, like $SH \cdot CH_2 \cdot CO \cdot NHPh$ itself, with $HgCl_2$ in OH, give the compound $Hg[S \cdot CH_2 \cdot CO \cdot NHPh]_2 \cdot HgCl_2$. The reported formation of an additive compound of cysteine and $AcCO_2H$ is not confirmed. In C_5H_5N a compound (II) (Zn derivative, $C_6H_7O_4NSZn \cdot 3H_2O$) is obtained of composition varying between that of $CO_2H \cdot CMe(OH) \cdot S \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$ and

$CO_2H \cdot CMe < \begin{smallmatrix} NH \\ S \cdot CH_2 \end{smallmatrix} > CH \cdot CO_2H$ (III), which with C_5H_5N yields the C_5H_5N salt, m.p. 100—101°, of (III). The reported prep. of an Ac_2 derivative is not confirmed. In Ac_2O - $AcOH$ - C_5H_5N , (II) gives the *Ac* derivative (IV), m.p. 225—226°, of (III), with the C_5H_5N salt, m.p. 160—162°, and the anhydride, m.p. 134—136°, of (IV). *o*- $C_6H_4Me \cdot NH_2$ gives the *o*-toluidide of (IV). α - $C_{10}H_7 \cdot NCO$ and (II) form the compound $C_{17}H_{16}O_5N_2S$. $AcCO_2H$ and $SH \cdot CH_2 \cdot CO_2H$ give *S*-carboxymethyl- α -thiol-lactic acid, m.p. 112—113°;

this with α -C₁₀H₇·NCO yields α -thiolacetic acid S-carboxy- α' -naphthylamide. The compound of SH·CH₂·CO₂H and BzCHO (A., 1936, 55) with AcOII·NaOAc yields the compound $\text{CHBz} \begin{smallmatrix} \diagup \text{O} \cdot \text{C} \diagdown \\ \diagdown \text{S} \diagup \end{smallmatrix} \text{CH}_2$, m.p. 93—94°. E. W. W.

Isomeric amylcarbamides and derived barbitals. J. S. BUCK and A. M. HJORT (J. Amer. Chem. Soc., 1937, 59, 2567—2569).—The following are prepared. *tert.*-Butyl-acetamide, m.p. 134°, and -malonic acid, m.p. 156°; *dl.*-sec.-amyl-, m.p. 144°, α -ethyl-*n*-propyl-, m.p. 193°, *dl.*-sec.-isoamyl-, m.p. 200°, and - β -methyl-*n*-butyl-carbamide, m.p. 125°; *dl.*-sec.-isoamyl-, m.p. 216°, β -methyl-iso-, m.p. >285°, and -*n*-butyl-amine hydrochloride, m.p. 180°; 5:5-diethyl-1-*n*-, m.p. 36°, -iso-, m.p. 78°, -sec., m.p. 35°, -sec.-iso-, m.p. 132°, and -*tert.*-amyl-, m.p. 75°, -1- α -ethyl-*n*-propyl-, m.p. 85°, - β -methyl-*n*-butyl-, m.p. 76°, and - β -methylisobutyl-barbituric acid, m.p. 112°. The min. hypnotic and lethal doses of the carbamides and barbiturates are listed. R. S. C.

Phosphine and arsine derivatives of silver and aurous halides.—See A., I, 65.

Compounds of platinum with unsaturated hydrocarbons of the ethylene series.—See A., I, 43.

Two reactions for detection of cyclopentadiene. A. P. TERENTIEV and M. I. IVANOVA (J. Gen. Chem. Russ., 1937, 7, 2087—2091).—The gas is passed into a solution of 30 g. of Hg(NO₃)₂ in 100 ml. of dil. HNO₃; a turbidity is obtained in presence of ≤ 0.25 mg. cyclopentadiene (I). Aromatic hydrocarbons, CMe₂·CH₂, (CHMe)₂, and (CH₂·CH)₂ do not interfere, but C₂H₂ gives a similar reaction. Alternatively, the gas is passed into 0.25% *p*-benzoquinone in EtOH, and a few drops of 10% KOH are added; a blue coloration appears in presence of ≤ 5 mg. of (I). C₂H₂ does not interfere. R. T.

Cracking of dicyclopentyl in presence of anhydrous aluminium chloride. J. K. JURIEV, R. J. LEVINA, and M. I. SPEKTOR (J. Gen. Chem. Russ., 1937, 7, 1581—1586).—The products obtained by heating dicyclopentyl with AlCl₃ at 170—290° contain cyclohexane about 35, cyclopentane 46, and paraffin hydrocarbons 18.5%. R. T.

Contact transformations of δ -cyclohexyl- Δ^a -butene. R. J. LEVINA and A. I. IVANOV (J. Gen. Chem. Russ., 1937, 7, 1866—1867).— δ -cyclohexyl- Δ^a -butene and Br in Et₂O give $\alpha\beta$ -dibromo- δ -cyclohexylbutane, b.p. 155°/13 mm., converted by heating with NaNH₂ at 160° into δ -cyclohexyl- Δ^a -butene. This yields PhBu^a and butylcyclohexane when heated with Pt on C. R. T.

1:4-Bisdiphenylmethylenecyclohexane. Stabilisation of linkings in rings. G. WITTIG and H. POOK (Ber., 1937, 70, [B], 2485—2491).—1:4-Bisdiphenylmethylenecyclohexane (I) is much more stable towards heat and alkali metals than is its acyclic analogue $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{a\alpha}$ -hexadiene, the linking becoming stabilised by being involved in a ring. Terephthalic acid, purified through the Et₂ ester, is smoothly hydrogenated to a mixture of the

cyclohexane-1:4-dicarboxylic acids when the suspension of its K salt in H₂O is hydrogenated under pressure in presence of a Ni-Co-Cu catalyst at 320°. Me₂ *trans*-cyclohexane-1:4-dicarboxylate in Et₂O is transformed by LiPh into *trans*-1:4-dihydroxydiphenylmethylenecyclohexane (II), m.p. 252—253.4°. *cis*-1:4-Dihydroxydiphenylmethylenecyclohexane (III), m.p. 195—196°, is derived similarly from the corresponding *cis*-ester. (II) is converted by boiling MeOH containing a little H₂SO₄ into *trans*-1:4-dimethoxydiphenylmethylenecyclohexane, m.p. 3053—07°, converted by K-Na followed by MeOH and H₂O into *trans*-1:4-dibenzhydrylcyclohexane (IV), m.p. 248—250°; analogous methods do not lead to the isolation of *cis*-1:4-dimethoxydiphenylmethylenecyclohexane, m.p. 174—176°, which is obtained from (III) and K phenylisopropyl and is transformed by K-Na into *cis*-1:4-dibenzhydrylcyclohexane, m.p. 224—225°. (II) or (III) with HCl in boiling AcOH affords (I), m.p. 258—260°. This is converted by K-Na in dioxan into (IV) in 70% yields, with unidentified hydrocarbon fractions, m.p. 146—147° (V), and m.p. 104.3—106°, respectively. For purposes of comparison Me₂ $\alpha\alpha'$ -dimethyladipate (mixture of isomerides) is converted by LiPh into a mixture, m.p. 219—223°, of the stereoisomeric $\alpha\zeta$ -dihydroxy- $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\beta\epsilon$ -dimethylhexanes, which is dehydrated to $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\beta\epsilon$ -dimethyl- $\Delta^{a\alpha}$ -hexadiene, m.p. 145—146° [not identical with (V)]. This is converted by K-Na in Et₂O followed by EtOH into CPh₂·CMe₂ or followed by CO₂ into $\gamma\gamma$ -diphenyl- β -methyl- Δ^b -butenoic acid, m.p. 119—121°. H. W.

Oxidation of hydrocarbons in the vapour phase. I. Aromatic hydrocarbons. II. Hydroaromatic hydrocarbons. J. K. CHOWDHURY and M. A. SABOOR (J. Indian Chem. Soc., 1937, 14, 633—637, 638—643).—I. Oxidation of C₁₀H₈ using as catalyst V₂O₅, Sn vanadate, Mn vanadate, Sn and V oxides, and Ni and Al oxides, gives phthalic (I) and maleic (II) anhydrides with small amounts of 1:4-naphthaquinone, BzOH, and C₁₀H₇·OH; the greatest activity is shown by mixed Sn and V oxides, and Sn vanadate. Phenanthrene is similarly oxidised to (I), with small quantities of (II), naphthalic anhydride, benzoquinone, and phenanthrol. The mechanism of the oxidation is suggested.

II. cycloHexane is oxidised to MeCHO, acraldehyde, AcOH, AcCO₂H, and some peroxides; temp. and flow of air influence the nature and yield of the products. Similar oxidation decahydronaphthalene gives (I) and (II), CH₂(CO₂H)₂, naphthaquinone, and CH₂O. F. R. S.

Alkylation with a hydrogenating catalyst. V. I. KOMAREWSKY (J. Amer. Chem. Soc., 1937, 59, 2715—2716).—Passage of C₂H₄ and C₆H₆ over Ni-Al at 350° gives PhMe (5%), C₁₀H₈ + Ph₂ (2%), and some H₂, CH₄, and C₂H₆; C₆H₆ alone gives only a little Ph₂ and traces of H₂; the alkylation is thus due to formation of PhEt, which is known to decompose under the experimental conditions. C₂H₄ and cyclohexane (I) over Ni-Al at 300° give PhMe (5%), CH₄, H₂, and C₂H₆; since (I) alone gives C₆H₆, the alkylation is preceded by dehydrogenation.

C_2H_4 alone gives C, H_2 , CH_4 , and C_2H_6 . Olefines are not formed in any of the reactions. R. S. C.

Contact isomerisation of ethylenic hydrocarbons. R. J. LEVINA (J. Gen. Chem. Russ., 1937, 7, 1587—1593).—Allylbenzene and *o*-, *m*-, and *p*-allyltoluene yield the corresponding propenyl derivatives when passed over floridin at 220—225°. Under such conditions, $(CH_2:CMc:CH_2)_2$ gives $(CMc_2:CH)_2$, and diallyl gives $(CHMc:CH)_2$.

R. T.

Liquid-phase reactions at high pressures.
II. Polymerisation of ethylenes. R. H. SAPIRO, R. P. LINSTAD, and D. M. NEWITT (J.C.S., 1937, 1784—1790).—Substances, $Ar:CR:CH_2$, but not $Ar:CR:CH_2R$, are readily polymerised at 100—150°/5000—10,000 atm. in absence of catalysts. The behaviour of $CPhMc:CH_2$ is studied in detail at 2000—10,000 atm.: at 100° up to 85% of polymeride (I) of mean mol. wt. 5400—5800 is formed, with very little lower polymeride; raising the temp. decreases both the yield and mol. wt. of the high polymeride and gives increasing amounts of lower polymerides; (I) is partly depolymerised at 125°. The unsaturated dimeride cannot be polymerised. Two modes of polymerisation are thus proved, viz., formation of (I) (main reaction at 100°) and of lower polymerides (significant at 125°). Dry HCl favours formation of lower polymerides, but not of (I); Bz_2O_2 diminishes formation of both. $ZnCl_2$ causes absence of (I) and formation of 90% of lower polymerides. Pouring (I) in C_6H_6 into MeOH ppts. it as fibres, but it is mainly hemicolloidal. At 100—150°/5000—10,000 atm. $CPhMc:CH_2$ gives only traces of dimeride, and $CH_2Ph:CH_2:CH:CH_2$ is almost unchanged. $CMe_2:CHMe$ gives no polymeride. $CPh_2:CH_2$ gives 35% of saturated (Br) dimeride, m.p. 100—105°. At 125°/5000 atm. $\alpha-C_{10}H_7:CMc:CH_2$ gives 1.9% of penta- to hexa-meride, but at 10,000 atm. affords 58% of (? amorphous) polymeride, sublimes at about 320° (decomp.) in a sealed tube, readily hydrolysed; 0.25% of dry HCl does not accelerate this reaction.

R. S. C.

Effect of oxygen and reduced nickel on the catalytic action of hydrogen bromide on the isomerisation of isostilbene to stilbene. Y. URUSHIBARA and O. SIMAMURA (Bull. Chem. Soc. Japan, 1937, 12, 507—509).—A direct influence on the isomerisation of isostilbene to stilbene is not exerted by O_2 or reduced Ni, but they co-operate with HBr, which is inactive by itself, in accelerating the change. It appears probable that in the presence of O_2 or Ni an active catalyst is formed from HBr. H. W.

Dissociation of hexa-*p*-alkylphenylethanes. M. F. ROY and C. S. MARVEL (J. Amer. Chem. Soc., 1937, 59, 2622—2625; cf. A., 1937, II, 373).—The % dissociation of compounds, $C_2(C_6H_4R-p)_6$, is found by the magnetic method to be $R = Et$ 3.5, Pr^s 4.2, Pr^s 4.5, Bu^s 4.9, $CHMeEt$ 5.9, and Bu^s 6.7. The increase in dissociation with increasing mol. wt. and branching of the chain is contrary to electronic ideas of Ingold. R. S. C.

Photosensitive nitro-compounds. N. N. VOROSHCHEV and V. V. KOZLOV (Prom. Org. Chim., 1937,

4, 399—406).—The work of the authors (1921—1937) is reviewed. R. T.

Mechanism of M. I. Kononov's reaction. I. A. I. TITOV (J. Gen. Chem. Russ., 1937, 7, 1695—1703).—PhMe and NO_2 yield mixtures of $CHPh(NO_2)_2$, $CH_2Ph:NO_2$, $C_6H_4Me:NO_2$, and $BzOH$, the yields and relative proportions of the products varying according to the temp. and duration of the reaction, and to the $[NO_2]$. Analogous results are obtained with PhMe and HNO_3 (*d* 1.4). The mechanism of the reaction is discussed. R. T.

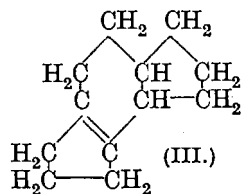
Isomerisation in cracking of hydrindene with aluminium chloride. M. B. TUROVA-POLLAK and F. I. PODOLSKAJA (J. Gen. Chem. Russ., 1937, 7, 1738—1741).—Hydrindene yields cyclopentane derivatives and methylcyclopentane when heated with $AlCl_3$ at 170—230°. R. T.

Cyclisation of dieneynes. IV. *trans*-1:2-Dialkyloctahydronaphthalene derivatives. G. A. NESTY and C. S. MARVEL. V. Hydrophenanthrenes. P. S. PINKNEY, G. A. NESTY, D. E. PEARSON, and C. S. MARVEL. Fused ring systems from dieneynes. VI. Limitations of the cyclisation reaction. P. S. PINKNEY and C. S. MARVEL (J. Amer. Chem. Soc., 1937, 59, 2662—2665, 2666—2668, 2669—2672; cf. A., 1936, 313).—IV. Syntheses of *trans*-1:2-dialkyloctahydronaphthalenes are described, the *trans*-structure being inferred from the resistance of the products to dehydrogenation. Addition of $MgEtBr$ and then of $COPr^s_2$ to 1-acetylenylcyclohexan-1-ol gives α -1-hydroxycyclohexyl- γ -*n*-propyl- Δ^1 -hexinen- γ -ol (I), m.p. 65—67°, dehydrated by $KHSO_4$ at 190—200° to α - Δ^1 -cyclohexenyl- γ -*n*-propyl-*n*-hex- Δ^s -en- Δ^s -inene, b.p. 98—100°/2 mm. (oxidises in air). This is hydrogenated (PtO_2 ; 3 atm.) in EtOH to α -cyclohexyl- γ -*n*-propyl-*n*-hexane, b.p. 83—85°/2 mm., and is cyclised by HCO_2H to 1-*keto*-4-ethyl-3-*n*-propyl-1:2:5:6:7:8:9:10-octahydronaphthalene, b.p. 107—108°/2 mm. (2:4-dinitrophenylhydrazones, m.p. 168—169°), converted by $Zn-Hg-HCl$ into 1-ethyl-2-*n*-propyl-3:4:5:6:7:8:9:10-octahydronaphthalene (II), b.p. 89—90°/2 mm., obtained also in poor yield from (I) by $Zn-Hg-HCl$. PtO_2 -hydrogenation of (II) gives 1-ethyl-2-*n*-propyldecahydronaphthalene, b.p. 79—89°/2 mm. Similar reactions starting from $COBu^s_2$ give α -1-hydroxycyclohexyl- γ -*n*-butyl- Δ^s -heptinen- γ -ol, m.p. 71.5—72.5°, α - Δ^1 -cyclohexenyl- γ -*n*-butyl-*n*-hept- Δ^s -en- Δ^s -inene, b.p. 112—113°/2 mm., α -cyclohexyl- γ -*n*-butyl-*n*-heptane, b.p. 95—96°/2 mm., 1-*keto*-4-*n*-propyl-3-*n*-butyl-1:2:5:6:7:8:9:10-octahydronaphthalene (III), b.p. 128—131°/2 mm. (2:4-dinitrophenylhydrazones, m.p. 156—157°), 1-*n*-propyl-2-*n*-butyl-3:4:5:6:7:8:9:10-octahydronaphthalene (IV), b.p. 109—110°/2 mm., and 1-*n*-propyl-2-*n*-butyldecahydronaphthalene, b.p. 98—100°/2 mm. The position of the ethylenic linking in the $C_{10}H_{18}$ derivatives is determined by ozonisation of (III) in CCl_4 to Bu^sCO_2H and 2-*n*-butyrylcyclohexane-1-carboxylic acid, b.p. 165—170°/2 mm. With Se at 365—390° (II) and (III) give blue liquids, containing Se, showing none of the ultra-violet absorption bands of $C_{10}H_8$ derivatives, but showing bands at

260, 267, and 273 μ ., characteristic of compounds having fused C_6H_6 and alicyclic rings.

V. Phenanthrene derivatives are obtained, but not always in good yield, and sometimes cyclisation fails. Di- Δ^1 -cyclohexenylacetylene (I), b.p. 105—110°/1.5 mm., m.p. < room temp., is obtained in 88% yield from di-1-hydroxycyclohexylacetylene (II) by $KHSO_4$ at 200—205°. With $Zn-Hg-HCl$ (II) or (much less readily) (I) gives $\Delta^{11:12}$ -dodecahydrophenanthrene, which gives with Se at 300—335° *trans-as*-octahydrophenanthrene, b.p. 94—95°/1.5 mm. The H_8 -compound is oxidised to o - $C_6H_4(CO_2H)_2$ and absence of $\alpha\alpha$ -pentamethylene-homophthalic acid indicates absence of the spirane. 1-Phenylacetylenylcyclohexanol (prep. from $CPh:C:MgBr$ and cyclohexanone in 66% yield) with PCl_5 gives 75% of phenyl- Δ^1 -cyclohexenylacetylene, b.p. 117—118.5°/1.5 mm., which with HCO_2H or $AcOH$ gives CH_2Ph Δ^1 -cyclohexenyl ketone (semicarbazone, new m.p. 170—171°) and no cyclic product. The ketone with H_2 -Raney Ni gives $\alpha\beta$ -dicyclohexylethyl alcohol; similar reduction of 9-keto- $\Delta^{11:12}$ -dodecahydrophenanthrene gives *tetra-decahydrophenanthr-9-ol*, b.p. 122—125°/1.5 mm. With H_2 - PtO_2 - Pt -black at 40—50 lb. in $AcOH$ (II) gives $\alpha\beta$ -di-1-hydroxycyclohexylethylene, m.p. 154—155°, but in $HBr-EtOH$ gives $\alpha\beta$ -dicyclohexylethane, m.p. 128—129°.

VI. The following reactions and those previously reported indicate the following necessities for ring formation from compounds containing $C:C:C:C$. At least one terminal C must carry a H; substitution must be sufficient to repress the rate of polymerisation; the $C:C$ may not be part of an aromatic ring; one, but not both, of the unsaturated linkings may be conjugated with an aromatic ring. cyclopentanone and $(C:MgBr)_2$ in Et_2O give 77% of di-1-hydroxycyclopentylacetylene (I), m.p. 107—108°, and traces of 1-acetylenylcyclopentanol (II), m.p. 20°, b.p. 65—65.5°/16 mm.; $(C:MgI)_2$ gives only 42% of (II) and much cyclopentylidenecyclopentanone. With $KHSO_4$ (I) gives di- Δ^1 -cyclopentenylacetylene, m.p. 58.5—60°, hydrogenated to $\alpha\beta$ -dicyclopentylethane, b.p. 109—110°/17 mm. With $Zn-Hg-HCl$ (I) or (II) gives a little 1:2:3:3a:4:5:6:7:8:8b-decahydro-as-indacene (III), b.p. 107—108°/17 mm.,



reduced by H_2 -Raney Ni to dodecahydro-as-indacene, b.p. 106—108°/18 mm. Only tars are obtained from (I) and (II) by H_2SO_4 and $AcOH$ or HCO_2H . 1-Hydroxycyclopentyl-1'-hydroxycyclohexylacetylene and $Zn-Hg-HCl$ give

3a:4:4a:6:7:8:9:9b-octahydro- α -naphthindane. 1-Hydroxy-1:2:3:4-tetrahydronaphthyl-1'-hydroxycyclohexylacetylene (prep. from 1-acetylenylcyclohexanol and 1-ketotetrahydronaphthalene), m.p. 85—95°, unstable, with $KHSO_4$ gives Δ^1 -cyclohexenyl-3:4-dihydro-1-naphthylacetylene, b.p. 170—172°/2 mm., which gives tars with acidic cyclising agents, but with $Zn-Hg$ affords 1:2:2a:3:4:5:6:6a:7:8-decahydrochrysene, b.p. 140—144°/1.5 mm., not converted into chrysene by Se. Di-3:4-dihydro-1-naphthylacetylene, m.p. 120—121°, obtained directly from

$(C:MgBr)_2$ and the ketone, could not be cyclised. $COBu^{\beta}-CH_2Ph$ leads to $\delta\eta$ -dibenzylidene- $\alpha\kappa$ -dimethyl- Δ^c -noninene, b.p. 179—180°/2 mm., which could not be cyclised. R. S. C.

Oxidation of anthracene and methylanthracene by chromic acid and by dilute nitric acid. M. A. ILJINSKI and E. S. POKROVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1937, 17, 111—115).—Variations in vals. obtained when anthracene (I) is determined in presence of methylanthracene (II) by CrO_3 oxidation are caused by variations in concn. of solvent $AcOH$. In conc. $AcOH$, some methylanthraquinone (III) is formed, and there is considerable destruction of the anthracene nucleus. In aq. $AcOH$ suspension, anthraquinone and (III) are, however, extremely stable. In dil. HNO_3 , (I) and (II) give only impure products. E. W. W.

Homologues of para-anthracene: polymerides of 9-methyl- and 9-ethyl-anthracene. A. WILLEMART (Compt. rend., 1937, 205, 993—994).—9-Methyl- and 9-ethyl-anthracene in Et_2O yield, on irradiation with the light of a Hg-vapour lamp, polymerides of high m.p., which when heated to the m.p. regenerate the original hydrocarbons. 9:10-Dimethyl-, 9-methyl-10-ethyl-, and 9-phenyl-anthracene do not polymerise. J. D. R.

Alkyl derivatives of anthracene. E. MARTIN (Ann. Off. nat. Combust. Liq., 1937, 12, 97—147).—The chemical and physical properties of the 9:10-dialkyl-, 9:10-dialkyl-9:10-dihydro-, and 9:9:10:10-tetra-alkyl-anthracenes and anthracene (I) are compared. Hydrogenation (Ni) of 9:10-diisobutyl-9:10-dihydroanthracene (II) gives 9:10-diisobutyl-1:2:3:4:5:6:7:8:9:10-decahydroanthracene, m.p. 86—87°. 9:9:10:10-Tetraisobutyldihydroanthracene is not hydrogenated at room temp. but higher temp. gives paraffins, alkyl-benzenes and naphthalenes. (I) and 9:10-dihydroanthracene form 1:2:3:4:9:10-hexabromo-1:2:3:4:9:10-hexahydroanthracene. 9:10-Diisobutylanthracene and (II) give 1:2:3:4-tetrabromo-9:10-diisobutyl-1:2:3:4-tetracene. The 9:9:10:10-tetra-alkyl-9:10-dihydroanthracenes do not react with Br in the dry state or in CCl_4 . The 9:10-dialkylanthracenes are oxidised by $HNO_3-H_2SO_4$ in the same manner as (I) and give anthraquinone. 9:9:10:10-Tetraisobutyl-9:10-dihydroanthracenes, however, are nitrated; e.g., 9:9:10:10-dihydroanthracene gives a 2:7-(NO_2)₂-derivative, m.p. 232—233°, identified by oxidation to 2:7-dinitroanthraquinone. Reduction gives 2:7-diamino-9:9:10:10-tetraisobutyl-9:10-dihydroanthracene, m.p. 158—160°. 9:10-Diisobutyl-9:10-disodioanthracene (III) with CO_2 gives 9:10-diisobutylanthracene-9:10-dicarboxylic acid; m.p. 255—257° (decomp.). (III) with H_2O leads to rearrangement to 9:9-diisobutyl-10:10-dihydroanthracene, m.p. 97—98°, also produced from (II) and $AlCl_3$ in the cold. On dehydrogenation with Br or benzoquinone this gem-dialkyl compound yields 9:10-diisobutylanthracene. The ultra-violet absorption spectrum of this hydrocarbon resembles those of 9:9-diethyl-10:10-dihydroanthracene and CH_2Ph_2 . D. J. B.

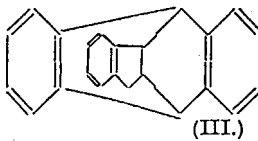
Dissociable anthracene oxides. Influence of meso-aliphatic groups. A. WILLEMART (Compt. rend., 1937, 205, 866—867; cf. A., 1937, II, 93).—9-Methyl-, 9:10-diethyl-, 9:10-dimethyl-, and 9-methyl-10-ethyl-anthracene, m.p. 144° (prepared from 9-methylanthrone and MgEtI), when insolated in CS₂ absorb 2 O per mol.; the photo-oxides decompose when gradually heated but do not liberate O₂. Rapid heating liberates a little O₂. J. L. D.

Reduction and hydrogenation of compounds of the 1:2-benzanthracene series. L. F. FIESER and E. B. HIRSCHBERG (J. Amer. Chem. Soc., 1937, 59, 2502—2509).—1:2-Benzanthracene (prep. in 61% yield from α -C₁₀H₇·CO·C₆H₄Me-o; Zn is a catalyst) with H₂-PtO₂ in EtOH containing a little FeCl₂ and HCl gives the 5:6:7:8-H₄-derivative, m.p. 88.5—89.5° [picrate, m.p. 156.5—157.5°; C₆H₃(NO₂)₃ compound, m.p. 159.5—160.5°], but with Na-iso-C₅H₁₁·OH gives the 1':2':3':4':9:10-H₆-compound, m.p. 69.3—69.9° [no picrate or C₆H₃(NO₂)₂ compound], also obtained from 1':2':3':4'-tetrahydro-1:2-benzanthracene by Na in xylene, followed by EtOH, or from 1':2':3':4'-tetrahydro-1:2-benzanthranlyl 10-acetate (I) by Zn dust, aq. NH₃, and PhMe. Catalytic hydrogenation of 10-methyl-1:2-benzanthracene (II) gives similarly the 5:6:7:8-H₄-derivative, m.p. 73.9—74.4° (picrate, m.p. 186—187°; gives a cryst. quinone, forming a quinoxaline derivative, m.p. 162—164°). 1':2':3':4'-Tetrahydro-1:2-benzanthr-10-one and MgMeCl give 10-methyl-1':2':3':4'-tetrahydro-1:2-benzanthracene, m.p. 117.3—117.8° (picrate, m.p. 161—162°), which by the Na-xylene-EtOH process gives 10-methyl-1':2':3':4':9:10-hexahydro-1:2-benzanthracene, an oil, unstable in air (oxidised to 1':2':3':4'-tetrahydro-1:2-benzanthraquinone), also obtained from (II) by Na-C₅H₁₁·OH or from the 9:10-H₂-compound [prepared from (II) by the Na-xylene-EtOH process], m.p. 94.4—94.9° (picrate, m.p. 112.5—113.5°; oxidised to 1:2-benzanthraquinone), by H₂-PtO₂ in EtOH-FeCl₃. Hydrogenation of 1:2-benzanthranlyl 10-acetate (III) in AcOH gives 5:6:7:8-tetrahydro-1:2-benzanthranlyl acetate, m.p. 159—159.5°, oxidised by CrO₃ to 10-acetoxy-5:6:7:8-tetrahydro-1:2-benz-3:4-anthraquinone, m.p. 232—233° (quinoxaline derivative, m.p. 276—278°). Prolonged hydrogenation of (III) gives 1':2':3':4':5:6:7:8-octahydro-1:2-benzanthranlyl acetate, m.p. 129.3—129.6°, also obtained by hydrogenation of (I). The hydrocarbons are usually better purified by way of the C₆H₃(NO₂)₃ compounds than of the picrates; they are best recovered from either by chromatographic absorption. 1:2-cyclopentano-5:10-aceanthrene is carcinogenic. Injection of (II) into mice gives tumours much more rapidly than does painting; the difference due to method of administration is less marked with other compounds. R. S. C.

Long life of excited organic molecules, exemplified by the rubrene oxidation.—See A., I, 40.

Indene group. I. Diene synthesis of anthra-indane. E. MAMELI (Gazzetta, 1937, 67, 669—681).—Anthracene (I) and excess of indene (II) combine at 200—211° in CO₂ to a 94—96% yield of

9:10-anthra-2':3'-indane [endo-2':3'-indano-9:10-anthracene] (III), m.p. 118° (98° ex C₆H₆), which is stable, in C₆H₆ or EtOH, to light or heat, is insol. in cold H₂SO₄, stable to Br or to dil. KMnO₄-Na₂CO₃, and,



unlike (II), does not react with Et₂C₂O₄-NaOEt or with PhCHO. CrO₃-H₂SO₄ oxidises (III) to anthraquinone and a substance, m.p. 202°. At 200—300°, (III) decomposes into (I) and (II). In fluorescence it resembles fluorene. C₆H₆, C₁₀H₈, or phenanthrene does not combine with (II). The structure of (I) is discussed. E. W. W.

Walden inversion. W. HÜCKEL [with, in part, E. KAMMENZ, A. GROSS, W. TAPPE, E. TIEDERMANN, and G. BECKER] (Annalen, 1937, 533, 1—45).—Walden inversion can be studied with compounds containing two asymmetric C, as the occurrence or absence of inversion depends on the energy difference between the complex of reactants and the stereoisomeric products and is thus independent of a second asymmetric centre. Further examples are provided that acylation with *p*-C₆H₄Me·SO₂Cl and C₅H₅N or hydrolysis of acetates does not cause inversion, but that production of acetates from *p*-toluenesulphonates by KOAc in EtOH, but less so in AcOH, involves inversion. The nature of the alcohol obtained by alkaline reduction or hydrogenation in acid of a cyclic ketone is correlated with the nature of the amine obtained from the corresponding oxime; existing data on these points and on the steric outcome of the reaction of an amine with HNO₂ are summarised and extended. In particular, new data are provided on the reaction of HNO₂ with amines of the decahydronaphthalene and hydrindane series and such regularities as exist are stressed. The possibility that *sec.* amines and HNO₂ give aliphatic diazo-compounds is refuted and it is concluded that reaction occurs by way of RN₂⁺, which breaks down to N₂ and R⁺. The outcome of the reaction may be (a) loss of H⁺ from R⁺ to yield an olefine, this being effected either by spontaneous decomp. or under the influence of a negative ion, (b) union of R⁺ and OH⁻ to give ROH, or (c) union of R⁺ and H₂O to give a complex [≥C·OH₂]⁺, which loses H⁺ to give ROH. These mechanisms can be applied to any reaction involving positive C ions. Simultaneous occurrence of (b) and (c) may account for partial inversions, or the alternative mechanisms (a)—(c) may account for the effect of solvent on the course of the reaction (evident with the *p*-toluenesulphonates but not with the amines). If R⁺ offers steric hindrance to the approach of OH⁻ or H₂O, then inversion is to be expected, since reaction will occur at other points of the mol. involving disturbance of the positions of the substituents (existence of such hindrance is to be judged from the reactivity of ROH and not from models). Such hindrance should, in the case of amines and HNO₂, lead to formation of relatively large amounts of olefines, but other factors, *e.g.*, ring size, also affect the amount. These conceptions are often, but not always, borne out by experience with amines. *p*-Toluenesulphonates and KOAc in

EtOH react by Bergmann's "negative mechanism" (approach of the reactant from the side of the C remote from the charge), but in AcOH the author's mechanism must also play a part.

Reactions marked * below involve inversion. *cyclo*-Pentylamine and HNO_2 give equal amounts of olefine and alcohol, but with *cyclohexylamine* the ratio of these two products is 1:5. With HNO_2 *trans*-decahydro- α -naphthylamine-I, m.p. -18° , gives * 70% of $\Delta^{1:9}$ - and *trans*- $\Delta^{1:2}$ -octahydronaphthalene and 30% of *trans*-decahydro- α -naphthol (I), m.p. 63° (with some of the isomeride, m.p. 49° , obtained without inversion). *trans*-Decahydro- α -naphthylamine-II, m.p. -1° , gives the related (I) and only traces of hydrocarbon. Similarly in glacial or dil. AcOH the *trans*- β -amine-II, new m.p. 15° (Bz derivative, m.p. 176 — 177° ; *hydrochloride*, decomp. 245 — 250°), gives quantitatively the alcohol (II), m.p. 75° , but the *trans*- β -amine-I, m.p. -47° (*hydrochloride*, decomp. 238°), gives 70% of *trans*- Δ^2 -octahydronaphthalene and (II) * with a little of the alcohol, m.p. 53° , formed without inversion. Results in the *cis*-series differ. Thus, *cis*-decahydro- α -naphthylamine-I, m.p. -18° , gives only the related alcohol, m.p. 93° ; about 7% of the same alcohol *, but 68% of *cis*-decahydro- α -naphthol-II, m.p. 55° , b.p. $118^\circ/12$ mm. (*phthalate*, m.p. 142°), and 25% of *cis*- $\Delta^{1:2}$ - (with a little $\Delta^{1:9}$ -) octahydronaphthalene are obtained from the *cis*- α -amine-II. *cis*-Decahydro- β -naphthylamine-I, m.p. 14° (*hydrochloride*, decomp. 270°), gives about 63% of the alcohol *, m.p. 18 — 31° , about 7% of the alcohol, m.p. 105° , and 30% of a mixture of *cis*- Δ^1 - and Δ^2 -octahydronaphthalene (under various conditions the speed, but not the course, of the reaction, varied), but the *cis*- β -amine-II (*hydrochloride*, decomp. 255 — 260°) gives * only the alcohol, m.p. 105° . The configuration of the 9-hydroxydecahydronaphthalenes is supported by cryoscopic data. α -Hydrindanyllamine-I (NH_2 in C_5 ring), m.p. -2° , gives 30% of *hexahydroindene* (unstable *nitrosochloride*, m.p. 102 — 106° ; *nitrol-piperidide*, m.p. 170°) and 70% of alcohol, mainly the liquid *cis*- α -hydrindanol-II* (II) (*phthalate*, m.p. 140°). The liquid *cis*- α -hydrindanyllamine-II (IV) (polymorphic benzoate, new m.p. 135°) gives 35% of a mixture of $\Delta^{1:9}$ - (cryst. *nitrosochloride*) and $\Delta^{1:2}$ -hexahydroindene, about 52% of (III), and 13% of α -hydrindanol *, m.p. 18° . β -Hydrindanyllamine-I (Bz derivative, m.p. 144°) gives the β -alcohol-II *, m.p. 10° (4 parts), the β -alcohol-I, m.p. 5° (1 part), and some hydrocarbon. *trans*- and *cis*-Decahydronaphthalene have m.p. -33° and -45° , respectively, and other physical data are also given. *trans*- β -Decaloneoxime and Na-EtOH give mainly the amine, m.p. 15° (gives *Me trans*-decahydro- β -naphthylcarbamate, m.p. 109°), but hydrogenation (Pt-black) of the ketone in EtOH- NH_3 gives mainly the amine-I (benzoate, m.p. 177°). The *H phthalate* of *cis*-decahydro- β -naphthol, m.p. 105° , has m.p. 116° ; and the *p*-toluenesulphonate gives forms, m.p. 44° and 76° (corr.) (stable). *cis*- α -Hydrindanols (OH in C_5 ring) with Na in decahydronaphthalene (V) give an equilibrium mixture containing about equal amounts of the two forms. However, *cis*-hydrindan-5-ol with Na in (V) and reduction of the ketone with

Na-EtOH give mainly *cis*-hydrindan-5-ol, m.p. 20° , with a little of the isomeride, m.p. 43° ; catalytic hydrogenation of the ketone gives only the second-mentioned alcohol. Hydrogenation (Pt-black) of α -hydrindoneoxime (OH in C_5 ring) in AcOH gives mainly the amine (Bz derivative, m.p. 180°), but also fair amounts of its isomeride. *cis*-5-Hydrindanyllamine-I (Bz derivative, m.p. 166°) has m.p. -19° . Hydrogenation (Pt-black) of *cis*- α -hydrindanoneoxime gives entirely the *cis*-amine-I, but with Na-EtOH 60—70% of (IV) is formed. *l*-Menthol *p*-toluenesulphonate and KOAc in abs. EtOH give a little *d*-neomenthyl acetate and Et ether with much Δ^3 -menthene; the ether and menthene are also obtained by heating in abs. EtOH alone or with CaCO_3 . The *p*-toluenesulphonate, m.p. 66° , of *trans*-decahydro- β -naphthol, m.p. 75° , with KOAc in abs. EtOH gives * much Δ^2 -octahydronaphthalene with decahydro- β -naphthyl Et ether and the acetate of the isomeric alcohol, m.p. 53° ; the sulphinate of the alcohol, m.p. 53° , is similarly inverted in EtOH. In AcOH only 15% of inversion occurs with the sulphonate, m.p. 66° ; considerable amounts of octahydronaphthalene are also formed.

R. S. C.

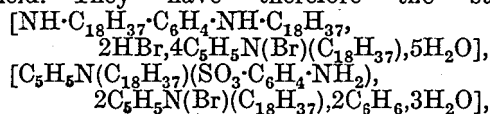
Alkanolamines. III. Reactions of chloronitrobenzenes with ethanolamines. M. MELTSNER, L. GREENSTEIN, G. GROSS, and M. COHEN (J. Amer. Chem. Soc., 1937, **59**, 2660—2661; cf. Kremer, A., 1937, II, 455).— o - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ and $\text{NH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$ at 175 — 180° give (o - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}$) $_2$ (I), o - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, and (?) *N*-*o*-aminophenylmorpholine, m.p. 200° . Addition of NaOH increases the yield of (I). o - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ and $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ in H_2O at 175° give o - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot[\text{CH}_2]_2\cdot\text{OH}$.

R. S. C.

Derivatives of glucamine and galactamine. H. P. DEN OTTER (Rec. trav. chim., 1937, **56**, 1196—1202).—Glucose anilide when reduced (Pd- H_2 or Al-Hg) yields NH_2Ph and no glucamine. The following are prepared by interaction of glucamine and the appropriate chloro- (or dichloro-) nitrohydrocarbon: *N*-2:4-dinitrophenyl-, m.p. 151 — 152° , *N*-2:4:6-trinitrophenyl-, m.p. 183° , *N*-2:4-dinitrophenyl-, m.p. 189° , and *N*-3-chloro-4:6-dinitrophenyl-glucamine, m.p. 181° . Similarly, from galactamine the following are prepared: *N*-2:4-dinitrophenyl-, m.p. 190° , *N*-2:4:6-trinitrophenyl-, m.p. 197° , *N*-3-chloro-4:6-dinitrophenyl-, m.p. 201° , and *N*-2:4-dinitronaphthyl-galactamine, m.p. 181° .

J. D. R.

Chemical and textile-chemical studies of new textile assistants and dyes. II. F. SEIDEL and A. BRÖSÄMLE (Ber., 1937, **70**, [B], 2497—2500).—The products obtained by the alkylation of aromatic mono- and di-amines by octadecyl bromide (cf. B., 1937, 116) and $\text{C}_5\text{H}_5\text{N}$ contain octadecylpyridinium bromide as constituent of the complex since when treated with picric acid they slowly give octadecylpyridinium picrate, m.p. 57 — 61° , in almost quant. yield. They have therefore the structures:



$[(C_6H_4 \cdot NH \cdot C_{18}H_{37})_2, 2HBr, 4C_6H_5N(Br)(C_{18}H_{37}), 3H_2O], [NH_2 \cdot C_{10}H_6 \cdot SO_3] [(C_6H_5N(C_{18}H_{37}))^+]$. The compound from aminoazobenzene gives *octadecylpyridinium nitrate*, m.p. 75–78° and after re-solidification, m.p. 238°, with dil. HNO_3 and hence is $[NPh \cdot N \cdot C_6H_4 \cdot N(C_{18}H_{37})_2, C_6H_5N(Br)(C_{18}H_{37}), 2HBr, 3H_2O]$. H. W.

Emeraldin sols.—See A., I, 79.

Manufacture of substituted 3-aminopyrenes.—See B., 1937, 1314.

Preparation of unsymmetrical fluorophenylthioureas.—See B., 1937, 1314.

Decomposition reactions of aromatic diazo-compounds. II. Reactions of benzenediazonium chloride. III. Non-ionic reactions of diazobenzene hydroxide. W. A. WATERS (J.C.S., 1937, 2007—2014, 2014—2016; cf. A., 1937, II, 97).—The decomp. of solid PhN_2Cl under $COMe_2$, C_6H_{14} , and CCl_4 yields HCl and $PhCl$; under EtI , some PhI is also formed. Decomp. in $COMe_2$ with $CaCO_3$ yields C_6H_6 and $CH_2Cl \cdot COMe$, and under these conditions Pb , Bi , Sn , Ni , Fe , Cu , and Ag are attacked to yield the metallic chlorides; Hg gives some $HgPhCl$, and Sb some $CPh_3 \cdot SbCl_2$. It is suggested that the salt $PhN_2^+Cl^-$ first undergoes rearrangement to $NPh \cdot NCl$, which then decomposes spontaneously with the formation of neutral Ph and Cl radicals and N_2 , or by a bimol. collision with the reagent. Dichloramine- T in dry $COMe_2$, C_6H_6 , or CCl_4 reacts with Hg , which supports the possibility of reaction by fission of the covalent $N \cdot Cl$ linking to give transient Cl atoms.

III. Decomp. of $PhN_2 \cdot OH$ in CS_2 yields $(PhS)_2$, and in *cyclohexane*, C_6H_6 and unidentified products. In absence of any other org. substance, Na benzenediazotate in H_2O decomposes to form a trace of C_6H_6 . It is suggested that $PhN_2 \cdot OH$ decomposes to neutral Ph and OH radicals, and N_2 , and the known oxidising reactions of $PhN_2 \cdot OH$ are discussed in connexion with this view. J. D. R.

Problem of racemate and racemic mixture. The optical antipodes of *cis*- β -decahydronaphthol. W. HÜCKEL and C. KÜHN (Ber., 1937, 70, [B], 2479—2484; cf. A., 1935, 80).—It is shown by the prep. of the pure optical antipodes that *cis*-2-decahydronaphthol, m.p. 18°, is a *dl*-mixture whilst the substance, m.p. 31°, is a racemic compound. *r-cis*-2-Decahydronaphthylamine is resolved into its optical antipodes by *d*-camphorsulphonic acid in $EtOH$. (+)-*cis*-2-Decahydronaphthylamine, m.p. 30.5°, gives a *d*-camphorsulphonate, $[\alpha]_D^{20} +31.45^\circ$ in $EtOH$, a *hydrochloride*, $[\alpha]_D^{20} -15.49^\circ$ in H_2O , a *Bz* derivative, m.p. 205°, $[\alpha]_D^{20} +1.72^\circ$ in $CHCl_3$, an α -bromo- π -camphorsulphonate, $[\alpha]_D^{20} +73.4^\circ$ in $EtOH$, and an *Ac* compound, m.p. 173°, $[\alpha]_D^{20} +21.44^\circ$ in $EtOH$. (−)-*cis*-2-Decahydronaphthylamine, m.p. 30.5°, affords a *camphorsulphonate*, $[\alpha]_D^{18} +15.14^\circ$ in $EtOH$, a *hydrochloride*, $[\alpha]_D^{20} -15.53^\circ$ in H_2O , a *Bz* derivative, m.p. 205°, $[\alpha]_D^{20} -1.68^\circ$ in $CHCl_3$, an α -bromo- π -camphorsulphonate, $[\alpha]_D^{19} +61.5^\circ$ in $EtOH$, and an *Ac* derivative, m.p. 173°, $[\alpha]_D^{20} -21.35^\circ$ in $EtOH$. The (+)-amine is transformed by HNO_3 into octahydronaphthalene, b.p. 84°/16 mm., 188°/760

mm., $\alpha_D^{20} +23.6^\circ$, and (+)-*cis*-2-decahydronaphthol-II, m.p. 38°, $[\alpha]_D^{20} +12.42^\circ$ in $EtOH$, $[\alpha]_D^{20} +3.94^\circ$ in C_6H_6 , $[\alpha]_D^{22.5} +4.24^\circ$ in *cyclohexane* (*H phthalate*, m.p. 146°, $[\alpha]_D^{20.8} -17.80^\circ$ in abs. $EtOH$, and its *Me* ester, m.p. 50°, $[\alpha]_D^{20} -10.22^\circ$ in $EtOH$; the corresponding optically inactive compound has m.p. 61° and is therefore a racemate). (−)-*cis*-2-Decahydronaphthol-II has m.p. 38°, $[\alpha]_D^{22.5} -12.41^\circ$ in $EtOH$; it gives a *H phthalate*, m.p. 146°, $[\alpha]_D^{20} +17.47^\circ$ in $EtOH$, and its *Me* ester, m.p. 50°, $[\alpha]_D^{18} +10.1^\circ$ in $EtOH$ (which is accompanied by a compound, m.p. 58°, $[\alpha]_D^{20} -1.66^\circ$ in $EtOH$). H. W.

Nitration of phenols by nitrous fumes. (SIGNA.) L. MONTI (Gazzetta, 1937, 67, 628—633).—Phenols are readily mononitrated by nitrous fumes when dissolved in light petroleum (b.p. 40—70°). From $PhOH$, *o*- remains in solution whilst *p*- $NO_2 \cdot C_6H_4 \cdot OH$ separates as an oil. *o*-Cresol yields, in solution, 3-nitro- and, as an oil, 5-nitro-*o*-cresol; with C_6H_6 or $AcOH$ as solvent, 3:5-dinitro-*o*-cresol is formed. *p*-Cresol yields, in petroleum, 3-nitro- and, in C_6H_6 , 3:5-dinitro-*p*-cresol. *m*-Cresol in either solvent gives 2-, 4-, and 6-nitro-*m*-cresol. Thymol in petroleum yields *p*- and, in solution, *o*-nitrothymol; both are also obtained in C_6H_6 . E. W. W.

Aromatic compounds of fluorine. XXIII. Attempted preparation of difluorinated phenols. G. SCHIEMANN and M. SEYHAN (Ber., 1937, 70, [B], 2396—2401).— o - $C_6H_4F \cdot OMe$ is nitrated to 2-fluoro-4-nitroanisole, m.p. 104.6°, reduced by Fe powder and conc. HCl at 100° to 2-fluoro-*p*-anisidine, m.p. 82.6°, which is diazotised and transformed into 3-fluoro-4-methoxybenzenediazonium borofluoride, decomp. 98°, dry decomp. of which affords 2:4-difluoroanisole, b.p. 52°/17 mm.; this is smoothly transformed by $AlCl_3$ in anhyd. C_6H_6 into 2:4-difluorophenol (I), b.p. 52—53°/19 mm., m.p. 22.4° (*Na* salt, m.p. 76°). The following processes are less suitable. o - $NH_2 \cdot C_6H_4 \cdot OEt$ is transformed through the diazonium borofluoride into o - $C_6H_4F \cdot OEt$ in 36% yield. This with HNO_3 (*d* 1.5) and $AcOH$ at 0° gives 2-fluoro-4-nitrophenetole, m.p. 78—80° (yield 28%), which is reduced by $SnCl_2$ and HCl to 2-fluoro-*p*-phenetidine, m.p. 239° (yield 55%). This gives only 17% yield of 3-fluoro-4-ethoxybenzenediazonium borofluoride, from which 2:4-difluorophenetole was obtained in very small yield: 2:4- $C_6H_3F_2 \cdot NO_2$ is converted into (I). *p*-Cresol is converted by HNO_3 (*d* 1.5) in $AcOH$ at 0° into 2:6-dinitro-*p*-cresol, m.p. 80—81° (61% yield), the *Na* derivative of which with Me_2SO_4 and $PhMe$ at 120—140° gives 2:6-dinitro-4-methylanisole, m.p. 122°; this is reduced to 2:6-diamino-4-methylanisole [*di*-hydrochloride, m.p. 241° (decomp.)], which gives a tetrazonium borofluoride, yielding a small amount of oil when decomposed. H. W.

Reaction between titanium tetrachloride and phenols. II. Reaction with chloro- and nitrophenols. G. P. LUTSCHINSKI (J. Gen. Chem. Russ., 1937, 7, 2044—2047).— $TiCl_4$ and *p*- $C_6H_4Cl \cdot OH$ afford *di*-*p*-chlorophenoxytitanium dichloride. *Di*-*o*- and *p*-nitrophenoxytitanium dichloride and *m*-nitrophenoxytitanium trichloride are obtained similarly from $TiCl_4$ and *o*-, *p*-, and *m*- $NO_2 \cdot C_6H_4 \cdot OH$. R. T.

2 : 4-Dibromo-*m*-anisidine and its derivatives. E. BUREŠ and S. JEŽEK (Chem. Listy, 1937, **31**, 464—470).—*Acet-m-anisidine*, m.p. 76°, in AcOH and Br yield 2 : 4-dibromo-3-acetamidoanisole, m.p. 150·5°, hydrolysed by KOH in EtOH to 2 : 4-dibromo-*m*-anisidine (I), m.p. 65° [Bz, m.p. 141°, and *Me* derivative, b.p. 159°; *hydrochloride*, m.p. 184—186° (decomp.); *sulphate*, m.p. 155° (decomp.)]. 3-*Chloro-*, m.p. 82°, and 3-*iodo-2 : 4-dibromoanisole*, m.p. 90°, were obtained from (I) by the Sandmeyer reaction. R. T.

2 : 6-Dibromo-3-aminophenetole, 2 : 4-dibromo-3-aminophenetole, and their derivatives. E. BUREŠ and Z. MANSFELD (Chem. Listy, 1937, **31**, 480—489).—*m*-Phenetidine and Br at room temp. yield 2 : 6-dibromo-3-aminophenetole, m.p. 47° [*hydrochloride*, m.p. 180—190° (decomp.); *sulphate*; *Ac*, m.p. 93°, *Ac*₂, m.p. 100°, *Bz*, m.p. 147°, and *Et* derivative, m.p. 71°], converted by the Sandmeyer reaction into 3-*chloro-*, m.p. 62°, 3-*iodo-*, m.p. 95°, or 3-*cyano-2 : 6-dibromo-*, m.p. 112°, or 2 : 3 : 6-*tribromo-phenetole*, m.p. 87°. *Acet-m-phenetidine*, m.p. 96—97°, in EtOH and Br yield 2 : 4-dibromo-3-acetamidophenetole, m.p. 156·5°, hydrolysed by aq. NaOH to 2 : 4-dibromo-3-aminophenetole, m.p. 54° (*hydrochloride*, decomp. at 200°; *sulphate*; *Ac*₂, m.p. 106°, *Bz*, m.p. 108°, and *Et* derivative, m.p. 62°), from which 3-*chloro-*, m.p. 56°, 3-*iodo-*, m.p. 86°, or 3-*cyano-2 : 4-dibromo-*, m.p. 97°, or 2 : 3 : 4-*tribromo-phenetole*, m.p. 77°, are obtained by the Sandmeyer reaction. R. T.

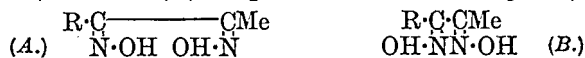
β-Arylaminoacrylic esters. I. Anisidinoacrylic ester and its reactions. M. V. RUBTZOVA (J. Gen. Chem. Russ., 1937, **7**, 1885—1895).—ONa·CH₂:CH·CO₂Et and *p*-anisidine in aq. AcOH yield *Et* trans-β-*p*-anisidinoacrylate (I), m.p. 120—121° (*N-Ac* derivative, m.p. 117—118·5°), whilst in aq. EtOH-AcOH the product is *Et*₂ *p*-anisidino-ββ'-*diacrylate* (II), m.p. 97—98° [*Br*₂-derivative, m.p. 195° (decomp.)], also obtained by heating (I) in vac. at 100°. The *cis-isomeride* (III), m.p. 57—57·5°, of (I) is prepared by boiling a CHCl₃ solution of (I) for 20 min., and adding the resulting solution to light petroleum. (III) when heated at 100° yields successively an intermediate compound, m.p. 99—101°, (I), and (II). The *N-Me* derivative, m.p. 37·5—39°, of (I) gives *p*-OMe·C₆H₄·NHMe, but not the expected quinoline derivative, when heated with SOCl₂. (II) when boiled with 10% in MeOH affords 1-*p*-anisyl-4-pyridone-3-carboxylic acid, m.p. 252° (*chloride*, m.p. 142·5—144°; *amide*, m.p. 225—226°; *diethylamide*, m.p. 118·5—119·5°; *Et* ester, m.p. 88—88·5°) from which 1-*p*-anisyl-4-pyridone, m.p. 110—111°, is obtained by distillation alone or from Zn dust. R. T.

Coupling of organic radicals by the action of Grignard reagents on heavy metal salts. II. Coupling of dissimilar radicals. J. H. GARDNER, L. JOSEPH, and F. GOLLUB (J. Amer. Chem. Soc., 1937, **59**, 2583—2584; cf. A., 1930, 76).—1 mol. each of MgPhBr and *p*-OMe·C₆H₄·MgBr with AgBr give 22—46·8% of Ph₂, 1·7—3·6% of (4-OH·C₆H₄)₂, and 4·7—8·2% of the "mixed" product, *p*-C₆H₄Ph·OH. R. S. C.

Synthesis of 3-substituted derivatives of methylcholanthrene. L. F. FIESER and B. RIEGEL

(J. Amer. Chem. Soc., 1937, **59**, 2561—2565).—The prep. of 1 : 6-NHAc·C₁₀H₆·OMe is modified. 6 : 1-OMe·C₁₀H₆·MgI and 7-cyano-4-methylhydrindene (I) in Et₂O·C₆H₆ give 7-6'-methoxy-1'-naphthoyl-4-methylhydrindene, m.p. 87·5—89° (softens at 82°), b.p. 260—265°/3 mm., converted by Zn at 400—405° into 3-methoxy-20-methylcholanthrene, dimorphic, m.p. 166—167·5° (softens at 161°) or mostly at 161° (*picrate*, m.p. 182·5°), which with HBr-AcOH gives 3-hydroxy-20-methylcholanthrene, m.p. 220·5—222° or 218—220° [*picrate*, m.p. 201—201·5° (decomp.)]. The conversion of β-C₁₀H₇NH₂ into its Ac derivative and thence into 1 : 6 : 2-C₁₀H₅Br₂·NHAc, m.p. 214·5—216°, 1 : 6 : 2-C₁₀H₅Br₂·NH₂·HCl, m.p. 120—121°, and 1 : 6-C₁₀H₆Br₂ (II), m.p. 56—57°, b.p. 175°/15 mm., is detailed. Grignard reactions with (II) attack either both Br or preferentially the Br in position 6. Thus condensation with (I) yields 7-5'-bromo-2'-naphthoyl-4-methylhydrindene, m.p. 102·5—105°, b.p. 246°/2 mm., converted at 270° into 4'-bromo-7-methyl-8 : 9-dimethylene-1 : 2-benzanthracene, m.p. 246·5—248° (no *picrate*). 2-C₁₀H₇NO₂ and Br in CHCl₃ give 5 : 2-C₁₀H₆Br·NO₂ and some *x*-bromo-2-nitronaphthalene, m.p. 98—102°. 5 : 2-C₁₀H₆Br·NH₂ gives 6-chloro-1-bromonaphthalene, m.p. 41—41·5° (no *picrate*), which with Mg and a little MgBu⁺Br gives the Grignard reagent; this with (I) affords 7-6'-chloro-1'-naphthoyl-4-methylhydrindene, m.p. 92—94°, b.p. 300°/20 mm., and thence at 400° 3-chloro-20-methylcholanthrene, m.p. 197—198·8° [(C₆H₅(NO₂)₃)₂ compound, m.p. 165·5—166·5°], converted by CuCN in C₅H₅N at 200—220° into the 3-CN-derivative, m.p. 243—251°. R. S. C.

isoEugenol and its polymerides. II, III. E. PUXEDDU and (SIGNA.) A. RATTU (Gazzetta, 1937, **67**, 647—654, 654—659; cf. A., 1937, II, 58).—II. *isoEugenol Pr^a* ether and KNO₂-AcOH give, in addition to dioximinodihydroisoeugenol *Pr^a* ether peroxide (I) (*loc. cit.*), new m.p. 85°, *isoeugenol Pr^a* ether nitrosite, C₁₃H₁₈O₅N₂, m.p. 127° (also obtained by Malagnini's method; A., 1895, i, 35), and a substance, m.p. 99·5°. *isoEugenol Et* ether similarly gives a nitrosite, m.p. 105°. Reduction of (I) by Zn-AcOH yields 3-methoxy-4-propoxyphenyl *Me* diketone α-dioxime (A), m.p. 139°, converted when heated into the β-dioxime (B), m.p. 178°. With HNO₃ (76%)



(I) gives a NO₂-derivative, m.p. 112°, and the corresponding *Et* ether (II) a NO₂-derivative, m.p. 102°. The *Br*-derivatives of (I) and of (II) have m.p. 94° and 115°, respectively.

III. Either ordinary or Schimmel's cryst. *iso*-eugenol, m.p. 32°, when treated with various polymerising agents gives the same cryst. polymeride (III), with an amorphous polymeride, also obtained when (III) is distilled at 20 mm. E. W. W.

[Similarity of] *o*-divinylbenzene and naphthalene. K. FRIES and H. BESTIAN (Annalen, 1937, **533**, 72—92).—4 : 5-Divinylpyrocatechol (I) resembles 2 : 3-C₁₀H₆(OH)₂ in not forming a quinone with Ag₂O in Et₂O, which indicates fixation of the ethylenic linkings as shown. 3 : 4-(OMe)₂C₆H₃[CH₂]₂·CO₂H

affords readily 3:4-(OMe)₂C₆H₃·[CH₂]₂·NH₂, b.p. 153°/12 mm., by way of the acid chloride, b.p. 152°/1 mm., m.p. 48°, azide, m.p. 52° (decomp.), (I.) and isocarbimide, m.p. 174°/16 mm., 142°/0.8 mm. (corresponding s-carbamide, m.p. 149°), and thence 6:7-dimethoxy-1-methyl-3:4-dihydroisoquinoline, which is best reduced to the 1:2:3:4-H₄-compound by H₂ in the presence of Ni-Cu-Co in EtOH at 80°/>1 atm. The H₄-base affords 6:7-dimethoxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline (II), which cannot be converted into (OMe)₂C₆H₃(CH₂)₂ owing to polymerisation. Hofmann degradation of the methiodide (III) of (II) gives a substance, which is hydrogenated to a mixture of isomerides, C₁₄H₂₃O₂N, b.p. 110—114°/0.2 mm., the cryst., mixed methiodides from which with Ag₂O afford dimethoxyethylstyrene, b.p. 90°/0.2 mm., hydrogenated to 4:5-dimethoxy-1:2-diethylbenzene, b.p. 85°/0.2 mm. With HI-red P-AcOH at 145° (II) gives 6:7-dihydroxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline, b.p. 128°/0.5 mm., m.p. 70° (Ac₂ derivative, m.p. 65°), which with Ag₂O gives 4:5-diethyl-o-benzoquinone, m.p. 76—86°. With HBr (III) gives 6:7-dihydroxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline methobromide, m.p. 227° (decomp.), the Ac₂ derivative, m.p. 257° (decomp.), of which is converted by Ag₂O into a mixture of isomerides, C₁₆H₂₁O₄N, b.p. 160—165°/0.4 mm.; the mixed methiodides, m.p. 225° (sinter at 178°), therefrom, when distilled with Ag₂O and sand, give 4:5-diacetoxy-1:2-divinylbenzene, m.p. 87° [tetrabromide, m.p. about 180° (decomp.)], converted by aq. alkali into (I), which polymerises readily and was not isolated. Hydrogenation of 3-NO₂·C₆H₄·CH:CH·CO₂H (improved prep.; 75% yield), m.p. 199°, gives only β-m-aminophenylpropionic acid; this is best obtained from the Na salt by H₂-Ni-Cu-Co in H₂O at 50°/1 atm. and is isolated as Bz derivative, m.p. 149°, which affords successively the chloride, m.p. 80—90° (decomp.) (amide, m.p. 154°), azide, m.p. 71.5° (decomp.) (s-carbamide, m.p. 219°), and β-m-benzamidodiphenylethylamine (IV), m.p. 111° [hydrochloride, m.p. 247° (decomp.)]; N-Bz derivative, m.p. 176°, and thence by 50% H₂SO₄ β-m-aminophenylethylamine, b.p. 156—157°/21 mm. [picrate, m.p. 204°; dihydrochloride, m.p. 308° (decomp.)]; Ac₂ derivative, m.p. 134°. The Ac derivative, m.p. 144°, of (IV) with P₂O₅ in boiling PhCl gives 75% of 6-benzamido-1-methyl-3:4-dihydroisoquinoline (V), m.p. 179° [phosphate, m.p. 239°; nitrate, m.p. 202° (decomp.)]; dihydrochloride, m.p. 309° (decomp.)], hydrolysed by KOH to 6-amino-1-methyl-3:4-dihydroisoquinoline, m.p. 131° [picrate, m.p. 216° (decomp.)]; dihydrochloride, m.p. 297° (decomp.)]. Hydrogenation (Ni-Cu-Co in EtOH at 100°/>1 atm. or PtO₂) of (V) gives 6-benzamido-1-methyl-1:2:3:4-tetrahydroisoquinoline, an oil [hydrochloride, m.p. 314° (decomp.)]; N-Bz derivative, m.p. 220°, which with CH₂O·HCO₂H gives 6-benzamido-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline (VI), m.p. 115° [hydrochloride, m.p. 225° (decomp.)], and thence the free 6-NH₂-compound, b.p. 124°/0.9 mm., m.p. 70° [picrate, m.p. 185° (decomp.)]; dihydrochloride, a hygroscopic glass]. The methiodide, m.p. 209°,

of (VI) with KOH-MeOH gives a mixture of isomerides, C₁₂H₁₈N₂, b.p. 115—125°/high vac. (hygroscopic dihydrochloride; oily Bz derivative), the Ac derivatives, b.p. 185—195°/0.9 mm., from which give an oily mixed methiodide. With KOH-MeOH this salt gives 3:4-divinylaniline, b.p. 100°/0.4 mm., which affords a (?) polymerised cryst. hydrochloride (no m.p.), is reduced to 3:4-diethylaniline, b.p. 146°/13 mm., and with SO₃H·C₆H₄·N₂Cl gives an abnormal insol. grey product. R. S. C.

Naphthalene series. I. Preparation of polyhydroxy-derivatives of naphthalene. S. N. CHAKRAVARTI and V. PASUPATI (J.C.S., 1937, 1859—1862).—Nitration of 2:6-C₁₀H₆(OMe)₂ (I) with HNO₃-AcOH yields 1-nitro-, m.p. 189°, and with HNO₃-AcOH-H₂SO₄ 1:5-dinitro-2:6-dimethoxynaphthalene, m.p. 265°, which are reduced (SnCl₂-EtOH) to 1-amino- [hydrochloride, m.p. 270° (decomp.)] and 1:5-diamino-, m.p. 192°, -2:6-dimethoxynaphthalene [hydrochloride, m.p. 265° (decomp.)], respectively. Similarly, 1-amino-, m.p. 83°, and 1:8-diamino-, m.p. 115°, -2:7-dimethoxynaphthalene, are prepared by nitration and reduction of 2:7-C₁₀H₆(OMe)₂. The Grignard reagent from 1:2-C₁₀H₆Br·OMe when treated successively with dry O₂ and BzCl-NaOH yields 2-methoxy-1-naphthyl benzoate, m.p. 110°. Bromination (Br-AcOH) of 2:6-C₁₀H₆(OH)₂ yields 1:5-dibromo-2:6-dihydroxynaphthalene, m.p. 233° [Me₂ ether, by Me₂SO₄-NaOH, m.p. 257°, also formed by bromination (Br-AcOH) of (I)]. Oxidation (K₂Cr₂O₇-H₂SO₄) of 1-amino-7-methoxy-2-naphthol hydrochloride yields 7-methoxy-1:2-naphthaquinone, m.p. 183°, reduced (SO₂-EtOH) to 1:2-dihydroxy-7-methoxynaphthalene, m.p. 127° (picrate, m.p. 156°; diacetate, m.p. 122°). Similarly, reduction (SO₂-H₂O) of 6- (II) and 7-hydroxy-1:2-naphthaquinone (III) yields 1:2:6-, m.p. 188° (triacetate, m.p. 262°), and 1:2:7-trihydroxynaphthalene, m.p. 197° (triacetate, m.p. 181—182°), respectively, which are methylated (MeI-K₂CO₃ in COMe₂) to 1:2:6-, m.p. 55° (picrate, m.p. 98°), and 1:2:7-trimethoxynaphthalene, an oil (picrate, m.p. 115°). Nitration (HNO₃-AcOH) of (II) and (III) yields 5-nitro-6-hydroxy-, m.p. 205°, and 8-nitro-7-hydroxy-, (IV), m.p. 210° (decomp.), -1:2-naphthaquinone, respectively, which are reduced by SO₂ to 5-nitro-1:2:6- (Me₂ ether, by MeI-K₂CO₃ in COMe₂, m.p. 93°) and 8-nitro-1:2:7-trihydroxynaphthalene, m.p. 220° [Me₂ ether (V), m.p. 98°], respectively. Reduction of (IV) with SnCl₂ gives 8-amino-1:2:7-trihydroxynaphthalene [hydrochloride, m.p. 270—275° (decomp.)], whilst similar reduction of (V) yields 8-amino-1:2:7-trimethoxynaphthalene [hydrochloride, m.p. 255° (decomp.)], converted by diazotisation and treatment with aq. KI into 8-iodo-1:2:7-trimethoxynaphthalene, m.p. 72°.

J. D. R.

Condensation of 4:4'-dihydroxydiphenylmethane with formaldehyde. I. P. LOSEV, K. A. ANDRIANOV, and O. J. FEDOTOVA (J. Gen. Chem. Russ., 1937, 7, 1828—1834).—CH₂(C₆H₄·OH-*p*)₂ is best prepared by the method of Voroshcov and Iuruigina (A., 1931, 937). It does not undergo polymerisation when heated at 180° in presence of HCl,

NaOH, or aq. NH_3 . It condenses with CH_2O in aq. EtOH-HCl , at the b.p., to give resinous products, from which 2 : 2'-dihydroxy-5 : 5'-di-(p-hydroxybenzyl)-diphenylmethane, m.p. 85—88°, was isolated.

R. T.

Dehydro-2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane. E. A. SHEARING and S. SMILES (J.C.S., 1937, 1931—1936).—The literature on the structure of dehydro-2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane (I) is reviewed critically. It is concluded that the conversion of (I) and similar substances into the dehydro-derivatives involves the removal of both mobile H atoms of the C_{10} nuclei, and that the CH_2 group is not directly concerned as is required by the structure assigned to (I) by Kohn and Ostersetzter (A., 1918, i, 501). The structure suggested by Pummerer and Cherbuliez (A., 1915, i, 417) is shown to be correct. When treated with Ac_2O or $\text{Ac}_2\text{O-AcCl}$, (I) is unchanged; with AcI in Ac_2O it yields 2 : 2'-diacetoxy-1 : 1'-dinaphthylmethane, and with $p\text{-C}_6\text{H}_4\text{Me-SO}_2\text{K}$ in aq. H_2SO_4 , a product, $\text{C}_{28}\text{H}_{22}\text{O}_4\text{S}$, m.p. 139—140° (decomp.). Nitration ($\text{HNO}_3\text{-Ac}_2\text{O}$) of (I) yields 4(?)-nitrodehydro-2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane, m.p. 166° [phenylhydrazone, m.p. 191° (decomp.)], whilst with MeMgI in C_6H_6 (I) gives the compound, m.p. 135°, recorded by Kohn and Ostersetzter (*loc. cit.*). Addition of Br to (I) in AcOH yields dehydro-2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane 3 : 4-dibromide, m.p. 148°, which is converted by $\text{C}_6\text{H}_5\text{N}$ into 3-bromo-2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane. Interaction of CH_2O and 6 : 2- $\text{C}_{10}\text{H}_6\text{Br-OH}$ in AcOH-HCl yields 6 : 6'-dibromo-2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane, m.p. 242° (decomp.) [diacetate (II), m.p. 287°; Na derivative], oxidised by HOCl to the dehydro-derivative, m.p. 209° (phenylhydrazone, m.p. 200°), which with $\text{AcI-Ac}_2\text{O}$ yields (II). Similarly from 3 : 2- $\text{C}_{10}\text{H}_6\text{Br-OH}$, 3 : 3'-dibromo-2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane (III), m.p. 207°, is formed, oxidised (HOCl) to the dehydro-derivative, m.p. 232°, which does not form a phenylhydrazone. 2-Hydroxy-2'-methoxy-1 : 1'-dinaphthylmethane (IV) treated with NaOCl in EtOH-NaOH yields 1'-chloro-, m.p. 147°, and with Br and AcOH-NaOAc , 1'-bromo-, m.p. 155°, -2'-keto-2-methoxy-1' : 2'-dihydro-1 : 1'-dinaphthylmethane, both of which when treated with AcOH-Zn regenerate (IV). Interaction of the Na salt of 2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane and Ac_2O yields 2-hydroxy-2'-acetoxy-1 : 1'-dinaphthylmethane, m.p. 195°, which with Br in AcOH-NaOAc yields 1'-bromo-2'-keto-2-acetoxy-1' : 2'-dihydro-1 : 1'-dinaphthylmethane, m.p. 127° (decomp.). Oxidation (NaOCl-NaOH) of 2 : 2'-dihydroxy-3 : 5 : 6 : 3' : 5' : 6'-hexamethyldiphenylmethane (V) yields a dehydro-derivative, m.p. 137°, and of 1-(2'-hydroxy-3' : 5'-dimethylbenzyl)-2-naphthol, a dehydro-derivative, m.p. 107° (phenylhydrazone, m.p. 167°). The following covalent Na derivatives are described : of (V), m.p. about 175°, of 6-bromo-2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane, m.p. about 215°, and of phenyl-2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane. Di-(2-hydroxy-3 : 5-dimethylphenyl)methane does not form a Na derivative.

J. D. R.

Dissociable organic oxides. Hydrogenation of photo-oxides. C. DUFRAISSE and J. HOUFILLART

(Compt. rend., 1937, 205, 740—743; cf. A., 1936, 1499).—The photo-oxides of tetraphenylnaphthacene (rubrene), meso-diphenylanthracene, and anthracene with H_2 -Raney Ni afford 5 : 12-dihydroxy-5 : 6 : 11 : 12-tetraphenyl-5 : 12-dihydronaphthacene, m.p. 308—309° (cf. A., 1931, 1052), 9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10-dihydroanthracene (cf. A., 1937, II, 332), and 9 : 10-dihydroxy-9 : 10-dihydroanthracene, m.p. 195° (cf. A., 1935, 487), respectively. Naphthacene is more difficult to reduce, but its reduction product is easily reduced further. Anthraquinone with H_2 -Raney Ni and alkali absorbs 6 H but only tetrahydroanthraquinone can be isolated as the diquinol is instantaneously oxidised in air.

J. L. D.

Derivatives of thiophloroglucinol. C. M. SUTER and G. A. HARRINGTON (J. Amer. Chem. Soc., 1937, 59, 2575—2578).—1 : 3 : 5- $\text{C}_6\text{H}_3(\text{SO}_3\text{Na})_3$ (modified prep.) and NaOH at 240—250°, best in Ni, give 77% of Na 3 : 5-dihydroxybenzenesulphonate, $+2\text{H}_2\text{O}$ [not converted into $s\text{-C}_6\text{H}_3(\text{OH})_3$ by NaOH; the Ac_2 derivative, hygroscopic, gives an intractable chloride], the Bz_2 derivative whereof affords resorcinol-5-sulphonyl chloride dibenzoate, m.p. 105°, reduced by Zn in boiling AcOH (not at 50°) to 5-thiolresorcinol dibenzoate, m.p. 110° (corresponding disulphide, m.p. 146°). This thiol with EtOH and a trace of NaOEt gives 5-thiolresorcinol, m.p. 88—89°, sublimes at 140°/1 mm., and with the alkyl halide and a trace of NaOEt in EtOH affords 5-methyl-, m.p. 78—78.5°, -ethyl-, m.p. 71—72°, -n-propyl-, m.p. 67—68°, -n-butyl-, m.p. 66°, -n-amyl-, m.p. 66°, and -n-hexyl-thiolresorcinol, b.p. 250°/1 mm. The PhOH coeffs. towards *S. aureus* and *E. typhi* of the alkylthiols are recorded; in general they increase with increasing mol. wt. of the alkyl substituent.

R. S. C.

Synthesis of a derivative of hydroxyquinol. M. MEYER (Compt. rend., 1937, 205, 920—922).—Prolonged interaction of $\text{OEt.CNa}(\text{CO}_2\text{Et})_2$ (1 mol.) with mesityl oxide (1 mol.) in PhMe-EtOH at room temp. and then at 50° affords an additive compound which is immediately cyclised and with HCl affords 2-ethoxy-2-carbethoxy-3 : 3-dimethylcyclohexane-1 : 5-dione, b.p. 126°/2 mm. [monosemicarbazone, m.p. 236° (block)], hydrolysed (large excess of NaOH) and simultaneously decarboxylated to 2-ethoxy-3 : 3-dimethyl-3 : 4-dihydroresorcinol, m.p. 85.5°. J. L. D.

Simultaneous dehydrogenation and dehydration with mixed catalysts. M. P. MASINA (J. Gen. Chem. Russ., 1937, 7, 2128—2136).—Zelinski's $\text{Ni-Al}_2\text{O}_3$ catalyst activates both dehydrogenation and dehydration of cyclohexanol and of methylcyclohexanol, at 260—380°. The intensity of dehydrogenation and polymerisation reactions rises with increasing Ni content of the catalyst. A $\text{Cr}_2\text{O}_3\text{-Cu-Al}_2\text{O}_3$ catalyst acted similarly to the above.

R. T.

Molecular structure and rate of reaction. W. HÜCKEL, H. HAVEKOS, K. KUMETAT, D. ULLMANN, and W. DOLL (Annalen, 1937, 533, 128—171).—Further observations of the rate of hydrolysis of the H succinates and H phthalates of the alcohols of the decahydronaphthalene and hydrindene series confirm the view (A., 1935, 41) that the simple reaction

kinetic considerations on which the Arrhenius equation is based have not the same theoretical importance with solutions as with gases. Configurative decisions based on physical data are not so significant with diastereoisomeric alcohols as with hydrocarbons. Further it is found that the good agreement between the methods of Vavon and Skita for the elucidation of configuration is not general. In doubtful cases the degree of association of the alcohol is not more useful than the rate of hydrolysis with which it is connected. The thermal stability of the toluenesulphonates is invariably parallel to the conditions of formation of diastereoisomeric alcohols. Those isomerides which are formed preferentially by catalytic hydrogenation in acid solution give toluenesulphonates which are unstable and decompose on long keeping or completely when boiled for about 1 hr. in MeOH into, among other products, unsaturated hydrocarbons. The esters of isomeric alcohols endure prolonged boiling with alcohol without giving appreciable quantities of hydrocarbons. Adopting Skita's arrangement, it appears that a substituent in the *cis*-vicinity to a strongly negative group tends to displace it, possibly with previous ionisation. Observations on models of the compounds under consideration are complicated by the mobility of the six-membered ring present in them. In consequence two substituents in the *cis*-position can be remote from one another by an angle between the *cis*-valencies not exceeding 72° and *trans*-substituents can approach to an angle of 48°. Herein lies a possible explanation of the unusual behaviour of α -alcohols with *cis*-union of rings. The Arrhenius formula $k = ae^{-q/RT}$ cannot be strictly applied. The rate of reaction of sterically unhindered alcohols in the case of succinates and phthalides approximates closely to that of the corresponding esters of cyclohexanol. The vals. $k_{40} = 1$ and $k_{60} = 0.1$ are readily recognised data for "normal" rates of succinates and phthalates. The view that the action consts. of alcohols with β -OH exceed those with α -OH and that the protection of the OH by the vicinal ring is thus directly evidenced could not be confirmed. In general the action consts. of esters reacting at the "normal" rate lie between 2 and 5×10^7 for succinates and phthalates. It is not universally true that high energy of activation causes a "steric hindrance" or, otherwise expressed, a particularly small rate of reaction, since many of the compounds with calc. relatively high energy react at the "normal" rate. Pronounced diminution of the rate is observed with only a few alcohols. High energy of activation and high action const. are frequently found simultaneously and their influences may compensate one another so that normal rates of reaction result. It is not possible to give general rules for the incidence of steric hindrance or for the relationship between energy of activation and action const. Among abnormal cases examples of simultaneous high energy of activation and high action const. are relatively frequent. *H* succinates are more rapidly hydrolysed than the corresponding *H* phthalates solely by reason of the greater energy of activation of the latter. These also are not hydrolysed at the same rates by NaOH and KOH; with the succinates this is not the case. The foaming power of the alkali phthalate solutions in-

dicates their presence partly as colloids and the proportion is probably not the same for the Na and K salts.

trans-1-Decahydronaphthol (I), m.p. 49°, is remarkable for its very small rate of reaction, possibly owing to very marked steric hindrance. In the decahydronaphthalene series apart from (I) the 1-alcohols have universally smaller rates of reaction than the 2-compounds. This is true of the α -hydroxyhydrindanes with OH in the six-membered ring, whereas those with OH in the five-membered ring behave "normally." The hydrindan- β -ols and decahydronaphth- β -ols are normal. *iso*Camphanol-II, m.p. 84°, although a primary alcohol, is exactly similar to the "normal" phthalates of the decahydronaphthols, whereas the isomeric *isocamphanol*-I, m.p. 101°, has so small a rate of reaction that it is comparable with *isoborneol*. *cyclo*Hexyl H succinate but not the H phthalate resembles the corresponding compounds of the dicyclic alcohols. In comparison with *cyclo*hexanol the rate of reaction of *o*-methyl*cyclo*hexanol is greatly diminished even when Me is in the *trans*-position. In respect of the Arrhenius formula the rate of reaction of *cis*-2-methyl*cyclo*hexanol is more dependent on the temp. at low than at high temp. whereas with the *trans*-compound the conditions are reversed. The experimental technique of the hydrolysis is described in detail. Many cryoscopic measurements and some determinations of heats of combustion are recorded.

Catalytic hydrogenation of *cis*-1-ketodecahydronaphthalene gives almost exclusively *cis*-decahydronaphth-1-ol, m.p. 93°, whilst similar treatment of *ar*-tetrahydronaphth-1-ol affords a complex mixture. *cis*-Decahydronaphth-1-ol-II, m.p. 55° (*H* succinate, m.p. 53—54°; *phenylurethane*, m.p. 80—81°; *p*-nitrobenzoate, m.p. 85—86°; *p*-toluenesulphonate, m.p. 89—90°), is therefore obtained from the corresponding amine. *cis*-Decahydronaphth-1-ol, m.p. 93°, gives a very unstable *p*-toluenesulphonate. The *H* phthalate, m.p. 107—108°, of *trans*-decahydronaphth-2-ol, m.p. 53°, is described. The *p*-nitrobenzoate, m.p. 56°, of 4-hydroxy-*cis*-hydrindane is reduced (PtO₂ in EtOH containing HCl) to the *p*-aminobenzoate, m.p. 179—181°, which is hydrolysed to the non-cryst. alcohol, b.p. 104°/12 mm. (*phenylurethane*, m.p. 82—83°; *H* succinate, m.p. 37°; *p*-toluenesulphonate, m.p. 53—54°). Similarly, the *p*-nitrobenzoate, m.p. 72°, of *cis*- α -hydrindanol is reduced to the *p*-aminobenzoate, which is hydrolysed to the alcohol, which gives a *H* succinate, dimorphous, m.p. 63° or 56—58°, and a very unstable *p*-toluenesulphonate, m.p. 54°. The non-cryst. α -hydrindanol-II gives a *p*-aminobenzoate, m.p. 83—84°, *p*-benzamidobenzoate, m.p. 146—147°, *H* succinate, m.p. 47°, and *p*-toluenesulphonate, m.p. 32—33°. The *H* succinates of the following decahydronaphthols are described (m.p. of alcohol first): *trans*- α -I, 49°, m.p. 107°; *trans*- α -II, 63°, m.p. 85°; *cis*- α -I, 93°, m.p. 66°; *cis*- α -II, 55°, m.p. 53—54°; *trans*- β -I, 53°, m.p. 64°; *trans*- β -II, 75°, m.p. 81°; *cis*- β -I, 105°, m.p. 81°, and *cis*- β -II, 18—31°, m.p. 54°; of the following hydrindanols; 4-hydroxy-*cis*-I, 16/31, m.p. 47°; 4-hydroxy-*cis*-II, liquid, m.p. 37°; 5-hydroxy-*cis*-I, 43°, m.p. 81.5°; 5-hydroxy-*cis*-II, 20°, m.p. 47°; β -*cis*-I, 5°, m.p. 71°; β -*trans*-, 21°, m.p.

58°; β -indanyl, cyclohexyl, and *Pr* ^{β} *H succinate* have m.p. 113°, 43°, and 51°, respectively. H. W.

Dehydration of 1- β -phenylethyl-3-methylcyclohexan-1-ol. D. PERLMAN and M. T. BOGERT (J. Amer. Chem. Soc., 1937, 59, 2534—2536).—Dehydration of 1- β -phenylethyl-3-methylcyclohexan-1-ol, m.p. about 25—26°; b.p. 145—146°/3—4 mm. [phenylurethane, m.p. 102—103° (corr.)], by 85% H₂SO₄ is accompanied by ring-closure and gives mainly 2-methyl-1:2:3:4:9:10:13:14-octahydrophenanthrene with some of the spiran $\text{CH}_2\text{--}\langle\text{CH}_2\text{--}\text{C}_6\text{H}_4\text{--}\text{C}\rangle\text{--}\langle\text{CH}_2\text{--}\text{CHMe}\text{--}\text{CH}_2\text{--}\text{CH}_2\text{--}\rangle\text{CH}_2$.

Neither product was isolated pure, but dehydrogenation by Se gives 2-methylphenanthrene and oxidation by CrO₃, followed by H₂O₂, gives some α -m-tolylhomophthalic acid, m.p. 140—142° (decomp.). The spiran is present mostly in the low-boiling portion of the crude product. R. S. C.

Introduction of the triphenylmethyl group.

IV. By-products formed during reactions with triphenylmethyl chloride. E. FUNAKUBO and T. MATSUI (Ber., 1937, 70, [B], 2437—2446).—The by-product obtained by the action of CPh₃Cl on isochavibetol and isoeugenol in C₅H₅N is CPh₃·OEt (cf. A., 1936, 1388). Reaction is never complete and the small amount of residual CPh₃Cl is not quantitatively transformed by H₂O into CPh₃·OH. CPh₃·OEt can arise from CPh₃Cl and EtOH or from CPh₃·OH and EtOH in presence of HCl but not in its absence. Reasons are advanced for the small and very variable yield of CPh₃·OEt. The "product," m.p. 81°, of van Alphen (A., 1927, 660) is probably CPh₃·OEt (cf. Schorigin, A., 1928, 59). H. W.

Condensations by sodium. IX. Preparation and properties of triphenyl- and trimethyl-triphenyl-carbinols and their derivatives. A. A. MORTON and W. S. EMERSON (J. Amer. Chem. Soc., 1937, 59, 1947—1949).—*p*-C₆H₄PhCl, Et₂CO₃, and Na powder in C₆H₆ (cf. A., 1932, 157) give 39% of (*p*-C₆H₄Ph)₃C·OH (I), reduced (SnCl₂, AcOH—conc. HCl) to tri-*p*-diphenylmethane (II), which with Br in CS₂ and sunlight affords the tetrabromide, (*p*-C₆H₄Ph)₃CB₄, m.p. 170—171° [hydrolysed by aq. alkali to (I)]. (II) with HNO₃ (*d* 1.6), conc. H₂SO₄, and 30% oleum gives a (NO₂)₃-derivative, m.p. 278—279° (decomp.). (II) could not be oxidised (CrO₃, AcOH). 4-Bromo-4'-methyl-diphenyl, Et₂CO₃, and Na similarly afford 23% of tri-(4'-methyl-*p*-diphenyl)-carbinol, m.p. 221—221.5° (chloride, m.p. 204—205°), reduced (method: Schmidlin and Garcia-Banús, A., 1913, i, 34) to tri-(4'-methyl-*p*-diphenyl)methane, m.p. 174—174.5° (tetrabromide, m.p. 99—103°). The above compounds show more intense colour reactions than the corresponding compounds of the CPh₃ series. H. B.

Dehydration of r - α -phenyl- β -o-, - m -, and - p -tolyl- $\alpha\beta$ -butylene glycols (" α "-forms). R. ROGER and A. M. ROBERTS (J.C.S., 1937, 1753—1761).— α -Phenyl- β -o- (I), m.p. 76—79°, - β - m - (II), m.p. 101—102°, and - β - p -tolyl- $\alpha\beta$ -butylene glycol (" α "-form) (III), m.p. 100—101°, obtained from COEt·CHPh·OH and the Mg derivatives of *o*-, *m*-, and *p*-C₆H₄MeBr, are dehydrated by dil. H₂SO₄, molten H₂C₂O₄, or Et₂O—HCl, by semihydrobenzoin trans-

formation, to α -phenyl- α -o- (IV), b.p. 176—178°/20 mm. (semicarbazone, m.p. 168—169°), - α - m - (V), b.p. 175—177°/18 mm. (semicarbazone, m.p. 164—165°; 2:4-dinitrophenylhydrazones, m.p. 169.5—170.5°), and - α - p -tolylbutaldehyde (VI), b.p. 170—173°/17 mm. (semicarbazone, m.p. 154—155°; 2:4-dinitrophenylhydrazones, m.p. 162—163°). With KOH—EtOH, (V) and (VI) give respectively α -phenyl- α - m -, b.p. 143—144°/17 mm., and - α - p -tolylpropane, b.p. 154—156°/23 mm.; (VI) is oxidised by CrO₃—AcOH to *p*-C₆H₄MeBz and *p*-C₆H₄Bz·CO₂H.

Dehydration by conc. H₂SO₄ is more complex, causing semipinacolinic transformation of (I) and (II), with the unexpected migration of Et, and respective formation of *r*-o- (VII), m.p. 39.5°, and *r*- m -tolyl α -phenylpropyl ketone (VIII), m.p. 82—83° (2:4-dinitrophenylhydrazones, m.p. 130—131° [accompanied by a compound (IX), m.p. 97—98°, containing S]). Synthetically, (VII) and (VIII) are prepared from CHPhEt·CN and *o*- and *p*-C₆H₄MeBr (Mg); (VIII) is not affected by boiling KOH—EtOH. Conc. H₂SO₄ converts (III), however, into α - p -tolylbutyrophenone (X), m.p. 54—55° (semicarbazone, m.p. 160—161°; 2:4-dinitrophenylhydrazones, m.p. 145.5—146.5°), with phenyl-*p*-tolylmethyl Et ketone (XI) (semicarbazone, m.p. 202.5—203.5°). Formation of (X) may be either by semihydrobenzoin migration of H or by vinyl dehydration; that of (XI) by semipinacolinic migration of *p*-C₆H₄Me. A mixture of (X) and (XI) on oxidation (CrO₃—AcOH) gives an acid, C₁₇H₁₆O₃, m.p. 138—139°, which may be derived from either. Synthetically, (X) is prepared from *p*-C₆H₄Me·COEt, reduced by Na—EtOH to *p*-C₆H₄Me·CHEt·OH, new b.p. 110°/21 mm. (and by Na—Hg to *s*-*p*-tolylethylpinacol, m.p. 101—102°), converted through α -chloro- α - p -tolylpropane, b.p. 94—95°/15 mm., into [Hg(CN)₂] α - p -tolylbutyronitrile, which with MgPhBr gives (X); (XI) is prepared from *p*-C₆H₄Me·CHPh·CN and MgEtBr.

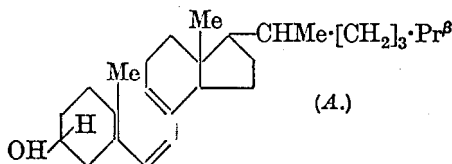
Conc. H₂SO₄ converts (IV) into (VII); (V) gives, not (VIII), but *r*- α - m -tolylbutyrophenone (?) (XII) (semicarbazone, m.p. 134—135°), with (IX); (VI) gives a mixture of (X) and (XI). Attempted prep. of (XII) from *m*-C₆H₄Me·CHEt·OH through α -chloro- α - m -tolylpropane, b.p. 104—106°/21 mm., gives [Hg(CN)₂] only *m*-propenyltoluene (?), b.p. 87—88°/25 mm. *m*-C₆H₄Me·CHPh·CN and MgEtBr give *r*-phenyl-*m*-tolylmethyl Et ketone (?) (semicarbazone, m.p. 161°).

From the migration of Et (above) it is concluded that the conversion of alkylhydrobenzoins by H₂SO₄ into alkyldeoxybenzoins (A., 1921, i, 565; 1923, i, 333) is the result of semipinacolinic migration of alkyl, and not of vinyl dehydration. Results with (I) suggest that in saturation capacity *o*-C₆H₄Me > Ph (cf. A., 1937, II, 190). In dehydrations by conc. H₂SO₄, aldehydes cannot always be regarded as intermediate products. E. W. W.

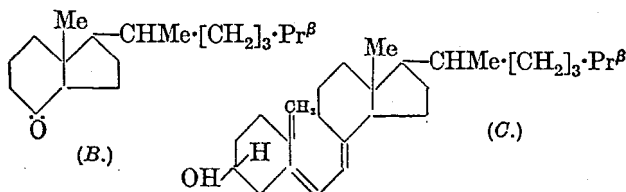
Photochemical dehydrogenation of 7-dehydrocholesterol and the pyrolysis of the product. Y. URUSHIBARA and T. ANDO (Bull. Chem. Soc. Japan, 1937, 12, 495—498).—7-Dehydrocholesterol [3:5-dinitrobenzoate, m.p. 212—212.5° (corr.; decomp.)] is dehydrogenated by prolonged insolation in EtOH—

C_6H_8 containing eosin to the "pinacol," $C_{54}H_{88}O_2$, m.p. 185.5–186° (corr.; decomp.), $[\alpha]_D^{25} -171^\circ$ in C_6H_5N , also $+1H_2O$, m.p. 184–185° (corr.; decomp.). This when heated at 185°/0.25 mm. and then distilled affords 10-demethylcholestatrien-3-ol, $C_{26}H_{40}O$, m.p. 76°, almost inactive optically $[3:5\text{-dinitrobenzoate}]$, m.p. 210.5–211° (corr.), $[\alpha]_D^{25} -3.8^\circ$ in $CHCl_3$. Similar dehydrogenation of 7-dehydrocholesteryl benzoate gives a product, $C_{68}H_{94}O_4$, m.p. 183–183.5° (corr.; decomp.), $[\alpha]_D^{25} -114^\circ$ in $CHCl_3$. H. W.

Substances obtained by irradiation of 7-dehydrocholesterol. A. WINDAUS, M. DEPPE, and W. WUNDERLICH (Annalen, 1937, **533**, 118–127).—Irradiation of 7-dehydrocholesterol (I) with ultra-violet light of $>280\text{ m}\mu$. gives lumisterol-3, $C_{27}H_{44}O$, m.p. 87–88° (from $COMe_2$) or m.p. 63–64° (from $MeOH$), $[\alpha]_D^{25} +197^\circ$ in $CHCl_3$ (dinitrobenzoate, m.p. 131°, $[\alpha]_D^{25} +20^\circ$ in $CHCl_3$; acetate, m.p. 131–132°, $[\alpha]_D^{25} +142^\circ$ in $CHCl_3$), which very closely resembles lumisterol (II) except in that it does not give an isolable compound with vitamin- D_3 whereas the compound from (II) and vitamin- D_2 is very characteristic. Constitutionally it probably differs from (II) only in the steric arrangement of groups at C_{10} . Irradiation of (I) with the ultra-violet light from Mg leads to non-cryst. tachysterol-3 (probably A), $[\alpha]_D^{25} -11.5^\circ$ in benzene (methylidinitrobenzoate, m.p. 137°,



$[\alpha]_D^{25} +40.4^\circ$ in $CHCl_3$), which, like tachysterol, combines with citraconic anhydride giving an adduct resolved into its components by heat. Vitamin- D_3 (III) is isolated as the 3:5-dinitrobenzoate, m.p. 128°, or (from Et_2O), m.p. 140°. The anisate, m.p. 114°, $[\alpha]_D^{25} +127^\circ$ in $CHCl_3$, and p-nitrobenzoate, m.p. 127°, $[\alpha]_D^{25} +114^\circ$ in $CHCl_3$, are described. Ozonisation of (III) gives a ketone (semicarbazone, $C_{19}H_{35}ON_3$, m.p. 214°) probably B, which supports formula C for (III).



H. W.

Sterols. XXIV. Sitostenone and stigmastenenone. R. E. MARKER and E. L. WITTE. XXV. *allo*Stigmasterols and *allositosterols*. R. E. MARKER and T. S. OAKWOOD. XXVI. Sitosteryl and stigmasteryl chloride and related compounds. R. E. MARKER and E. J. LAWSON. XXVII. *epi*Sitosterol and *epistigmasterol*. R. E. MARKER, E. J. LAWSON, E. L. WITTE, and T. S. OAKWOOD (J. Amer. Chem. Soc., 1937, **59**, 2704–2708, 2708–2710, 2711–2713, 2714–2715; cf. A., 1938, II, 12).—XXIV. The identity of tallol-sitosterol, termed simply sitosterol (I), with 22-dihydrostigma-

sterol is confirmed. With pptd. Cu at 150–200°/2 mm. (I) gives sitostenone, hydrogenated (PtO_2 ; 3 atm.) in Et_2O to 24-ethylcoprostanol (II), m.p. 137° (acetate, m.p. 94°), also obtained similarly from stigmastenenone and oxidised by CrO_3 to 24-ethylcoprostanone (III), m.p. 114°. With $Al(OPr^i)_3$ this ketone gives 24-ethylcoprostan- β -ol, m.p. 127° (acetate, m.p. 89°) [and some (II)], which is epimerised to (II) by Na in xylene. With Br and a drop of HBr in AcOH (III) gives the 4-Br-derivative, m.p. 149°, converted by C_6H_5N into sitostenone, which is reduced by $Na-C_5H_{11}OH$ to sitostanol, identical with stigmastanol (IV) (acetate, m.p. 136°). Stigmastanol and $Na-C_5H_{11}OH$ give 5:6-dihydrostigmastanol [acetate, m.p. 122° (dibromide)] and a (?) hydrocarbon, m.p. 72°; the 5:6- H_2 -compound gives (IV) when hydrogenated.

XXV. *epiallo-* (V) and *allo-Sitosterol* (VI) and *allo-stigmasterol* (VII) are prepared. All are readily dehydrated and *epiallostigmasterol* (VIII) is too unstable for isolation in a pure state. Stigmastenenone with $Al(OPr^i)_3$ gives (VI), m.p. 137° (digitonide), the acetate, m.p. 132°, of which gives (II) when hydrogenated and hydrolysed; the mother-liquors afford a mixture of (VIII) and its dehydration product, also reduced to (II). Sitostenone gives similarly (VI), m.p. 158° (digitonide), and (V), m.p. 138°, the acetates, m.p. 88° and 92°, respectively, of which are hydrogenated to (II).

XXVI. PCl_5 and (I) give sitosteryl chloride, m.p. 86° (dibromide, m.p. 96°), hydrolysed by $KOAc-AcOH$ to sitosteryl acetate and hydrogenated (PtO_2) in Et_2O to α -sitostyl [α -stigmastyl] chloride, m.p. 107°, which is also obtained by hydrogenation of stigmasteryl chloride (prep. by PCl_5 , m.p. 83° (dibromide, m.p. 182°), from *epistigmastanol* by PCl_5 , and from stigmastanol by $SOCl_2$. β -Sitostyl [β -stigmastyl] chloride, m.p. 118°, is obtained from stigmastanol or sitostanol and PCl_5 or from *epistigmastanol* and $SOCl_2$, and is hydrolysed to stigmastanol. The α -chloride is hydrolysed by $KOAc$ in $BuCO_2H$ to *epistigmastanol* and with $Na-C_5H_{11}OH$ gives stigmastane [sitostane], m.p. 84°.

XXVII. The Grignard reagent from sitosteryl chloride with dil. H_2SO_4 gives (I) and *episitosterol*, m.p. 135° (acetate, m.p. 66°), hydrogenated to *epistigmastanol*. Stigmasteryl chloride similarly affords *epistigmasterol*, m.p. 151° (acetate, m.p. 98°), reduced to *epistigmastanol*. Both new *epi*-compounds are readily dehydrated.

R. S. C.

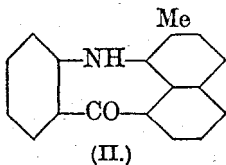
Vitamin-E. Tocopherols from various sources. O. H. EMERSON, G. A. EMERSON, A. MOHAMMAD, and H. M. EVANS (J. Biol. Chem., 1937, **122**, 99–107).— α -Tocopherol is isolated from cottonseed oil, lettuce leaves, and palm oil. Its absorption spectrum is revised. Two additional tocopherols have been isolated, β -tocopherol as *allophanate*, $C_{31}H_{52}O_4N_2$ or $C_{30}H_{50}O_4N_2$, m.p. 144–146°, $[\alpha]_D^{25} +5.7^\circ$ in C_6H_6 , from wheat-germ oil, and γ -tocopherol as *allophanate* (isomeric with the β -compound), m.p. 138–140°, $[\alpha]_D^{25} +3.4^\circ$ in C_6H_6 , from cottonseed oil and probably also from palm oil. β - and γ -Tocopherol are half to one third as active biologically as α -tocopherol.

R. S. C.

Action of metals on acid chlorides. G. A. VARVOGLIS (Ber., 1937, **70**, [B], 2391—2396).—The action of Zn on BzCl in Et₂O gives unchanged Zn, and mainly EtOBz with EtCl, BzOH, CH₂Ph·OH, and ZnCl₂. After removal of these substances a small quantity of viscous residue (I) remains in which benzil or isobenzil could not be detected. The initial change is between the acid chloride or a mol. compound of it with Et₂O and Zn and leads to ZnCl₂; the Bz residues do not unite to benzil but are involved in a complex manner in the formation of (I). The ZnCl₂ thus produced accelerates the change between BzCl and Et₂O to EtCl and EtOBz, which occurs also in absence of ZnCl₂. A third reaction is the reduction of BzCl to CH₂Ph·OH. The liberation of H is proved by the formation of quinol dibenzoate (II) and chloroquinol dibenzoate (III) from Zn and BzCl in Et₂O containing *p*-benzoquinone (IV). In isoamyl ether and dioxan, respectively, the main products are isoamyl benzoate or glycol dibenzoate, respectively; the latter is not produced in presence of (IV), its place being taken by (II) and (III). In C₆H₆, CS₂, or CCl₄ the only change is a slight conversion of the chloride into the acid. In C₆H₆ containing (IV) there is a considerable production of (III) and particularly of (II); the change is probably due to a catalytic action of ZnCl₂ formed in small amount on C₆H₆ and BzCl in the sense of a Friedel-Crafts reaction. (The presence of COPh₂ could not be detected.) A similar change is observed in anisole. Fe powder behaves similarly to Zn. AcCl resembles BzCl but gives a greater proportion of (I). H. W.

Bromo-derivatives of novocaine. III. L. FREJKA and L. ČIZMÁŘ (Chem. Listy, 1937, **31**, 460—464).—3-Bromoacet-*p*-toluidide in 2.5% aq. MgSO₄ and KMnO₄ at 70° yield 3-bromo-4-acetamidobenzoic acid, m.p. 228—229°, hydrolysed by cone. H₂SO₄ to 3-bromo-4-aminobenzoic acid, m.p. 218—219° (Et ester, m.p. 90—91°; Pr^a ester, m.p. 58—59°), which with OH·CH₂·CH₂Cl gives β-chloroethyl 3-bromo-4-aminobenzoate, m.p. 100°. This yields β-diethylaminoethyl 3-bromo-4-aminobenzoate (I), m.p. 157—158°, with NH₄Et₂ at 105—110° (10 hr.). (I) is also obtained by gradual addition of Br in Et₂O to an aq. solution of novocaine in sunlight. R. T.

o-2-Methyl-1-naphthylaminobenzoic acid. W. KNAPP (Monatsh., 1937, **71**, 122—127).—2:1-C₁₀H₆MeBr and o-NH₂·C₆H₄·CO₂H are transformed by anhyd. K₂CO₃ and Cu powder in boiling PhNO₂ into o-2-methyl-1-naphthylaminobenzoic acid (I), m.p. 215—216° (incipient decomp.), converted by P₂O₅ in boiling PhMe into phenyl 2-methyl-8-naphthyl ketone o:1-imine (II), m.p. 196—197°, and a methylbenzacridone, m.p. 337—339°. At somewhat above its m.p. (I) is converted into phenyl-2-methyl-1-naphthylamine, m.p. 121—122°. H. W.



Effects of oxygen and peroxides on the rate of addition of bromine to cinnamic acid in carbon tetrachloride. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1937, **12**, 499—506).—The effect of O₂ on the addition of Br to

CHPh:CH·CO₂H in CCl₄ has been established. In presence or absence of O₂ the reaction between Br and CHPh:CH·CO₂H in CCl₄ is not affected by HBr. Bz₂O₂ accelerates the addition. In all cases, in a vac. or in presence of O₂, Bz₂O₂, or HBr the product which separates is cinnamic acid dibromide, m.p. 198°. The experiments are performed in the dark at room temp. H. W.

Some derivatives of diphenylamine and a new synthesis of N-arylanthranilic acids and of acridones. (Miss) M. M. JAMISON and E. E. TURNER (J.C.S., 1937, 1954—1959).—Application of the method of Chapman (A., 1929, 550) yields the following: N-o-chloro-, m.p. 59—60°, N-2:4-dichloro-, m.p. 81°, and N-p-bromo-phenylbenzimidino-p-chlorophenyl ether, m.p. 83—84°, and N-2:4-dichloro-phenylbenzimidino-2:4:6-trichlorophenyl ether, m.p. 86—88°. When heated these give N-benzoyl-2:4-dichloro-, m.p. 115°, -2:4:4'-trichloro-, m.p. 117—118°, -4-chloro-4'-bromo-, m.p. 149°, and -2:4:6:2':4'-pentachloro-diphenylamine, m.p. 160°, respectively, which are hydrolysed to 2:4'-dichloro-(I), m.p. 42°, 2:4:4'-trichloro-(II), m.p. 67—68°, 4-chloro-4'-bromo-, m.p. 91.5°, and 2:4:6:2':4'-pentachloro-diphenylamine, m.p. 94°, respectively. Interaction of 1:2:4-OH·C₆H₃Cl₂ and N-p-chlorophenyl-*p*-toluanilideiminochloride (from *p*-tolu-*p*-chloroanilide and PCl₅) yields N-p-chlorophenyl-*p*-toluimino-2:4-dichlorophenyl ether, a glass, which when heated gives N-p-toluoyl-2:4:4'-trichlorodiphenylamine, m.p. 157°. Similarly, benz-*p*-chloroanilideiminochloride (III) and *l*-menthyl salicylate give N-p-chlorophenylbenzimidino-2'-(carbo-*l*-menthoxy)phenyl ether, a glass; this when heated yields N-benzoyl-4-chloro-2'-(carbo-*l*-menthoxy)diphenylamine, which immediately decomposes at the formation temp. into *l*-menthene, BzOH, and 3-chloroacridone (IV). Nitrosation (Fischer, A., 1878, 313) of *p*-chlorodiphenylamine and of (I) yields respectively, N-nitroso-*p*-chloro-, m.p. 88°, and N-nitroso-2:4'-dichloro-diphenylamine, m.p. 66—67°, which are reduced (Zn-aq. EtOH·AcOH) to N-phenyl-N-p-chlorophenyl-, b.p. 174°/2 mm., and 2:4'-dichloro-NN-diphenylhydrazine (V), b.p. 241°/8 mm., respectively. (V) with 4-chlorophthalic anhydride yields N-2-chlorophenyl-N-4'-chlorophenyl-N'-N'-4-chlorophthalylhydrazine, m.p. 142—142.5°. 2:4:4'-Trichlorodiphenylcarbonyl chloride, m.p. 117—118°, is obtained from (II) and COCl₂ at 150—200°. Me salicylate (VI) and (III) with NaOEt give N-p-chlorophenylbenzimidino-o-carbomethoxyphenyl ether, m.p. 130—131°, which at 300° is converted into Me N-benzoyl-4-chlorodiphenylamine-2'-carboxylate, m.p. 139—140°; this is decomposed at 320° into MeOBz and (IV), and hydrolysed by NaOH in aq. EtOH to N-benzoyl-4-chlorodiphenylamine-2'-carboxylic acid, m.p. 191—192° [also decomposed by heat to BzOH and (IV)], and by cone. aq. NaOH to 4-chlorodiphenylamine-2'-carboxylic acid [also converted into (IV)]. Benz-2:4-dichloroanilideiminochloride and (VI) yield N-2:4-dichlorophenylbenzimidino-o-carbomethoxyphenyl ether, m.p. 85—87° converted at 280° into Me N-benzoyl-2:4-dichlorodiphenylamine-2'-carboxylate, m.p. 114—116°, which is hydrolysed successively to

N-benzoyl-2 : 4-dichlorodiphenylamine-2'-carboxylic acid, m.p. 177°, and to 2 : 4'-dichlorodiphenylamine-2'-carboxylic acid. Similar reactions yield 4-*m*-xylylbenzimidino-2'-carbomethoxyphenyl ether, m.p. 87—88° [isomerised at 275° to *Me N*-benzoyl-2 : 4-dimethyldiphenylamine-2'-carboxylate, m.p. 132—133° (no acridone formed at 350°), which is hydrolysed to *N*-benzoyl-2 : 4-dimethyldiphenylamine-2'-carboxylic acid, m.p. 192—193° (gives 1 : 3-dimethylacridone at 300°)], and *N*-phenylbenzimidino-*o*-carbomethoxyphenyl ether, m.p. 110—111°, isomerised at 275° to *Me N*-benzoyldiphenylamine-2-carboxylate, m.p. 132—133°, which is partly hydrolysed to *N*-benzoyl-*N*-phenylantranilic acid, m.p. 186°. From *Me* 3 : 5-dibromosalicylate and benz-*p*-bromoanilideiminochloride is obtained *N*-*p*-bromophenylbenzimidino-4' : 6'-dibromo-2'-carbomethoxyphenyl ether, m.p. 105°, converted at 270° into *Me N*-benzoyl-4 : 6 : 4'-tribromodiphenylamine-2-carboxylate, m.p. 138—139°, successively hydrolysed to *N*-benzoyl-4 : 6 : 4'-tribromodiphenylamine-2-carboxylic acid, m.p. 217—218°, and 4 : 6 : 4'-tribromodiphenylamine-2-carboxylic acid, m.p. 222°, which with POCl₃ in boiling xylene yields 1 : 3 : 7-tribromoacridone, m.p. >300°. *N*-*p*-Methoxyphenylbenzimidino-*p*-chloro-*o*-carbomethoxyphenyl ether, m.p. 105—106° (from *Me* 5-chlorosalicylate and benz-*p*-anisidideiminochloride), by the same series of reactions gives *Me N*-benzoyl-4-chloro-4'-methoxydiphenylamine-2-carboxylate, m.p. 164°, and *N*-benzoyl-4-chloro-4'-methoxydiphenylamine-2-carboxylic acid (softens and loses 0.5C₆H₆ at 120—125°; no sharp m.p.; converted at 300° into 3-chloro-7-methoxyacridone, m.p. >300°). *N*-*p*-Chlorophenylbenzimidino-*p*-carbomethoxyphenyl ether, m.p. 78—79° (from benz-*p*-chloroanilideiminochloride and *p*-OH·C₆H₄·CO₂Me), similarly gives *Me N*-benzoyl-4-chlorodiphenylamine-4'-carboxylate, m.p. 140—141°, hydrolysed to *N*-benzoyl-4-chlorodiphenylamine-4'-carboxylic acid, m.p. 223—224°.

J. D. R.

Configuration of cyclic 1 : 1-hydroxycarboxylic acids. J. BÖESEKEN and (MLLE.) F. J. VAN BUUREN (Rec. trav. chim., 1937, 56, 1211—1218).—Measurements of the increase in the conductivity of H₃BO₃ solutions caused by the addition of 1-hydroxycycloheptane-, -hexane-, -pentane-, -butane-, and -propane-1-carboxylic acid shows that with rings of 4 C atoms, the relative positions of the OH and CO₂H are the same as in the open-chain hydroxy-carboxylic acids. In rings of 3 or 4 C, the angle between the OH and the CO₂H is increased by distortion, and the increase in the conductivity of H₃BO₃ solutions is very much diminished. Hydroxycyclobutanecarboxylic acid readily forms a lactide, even in H₂O, and conductivity measurements in presence of this acid are only approx.

J. D. R.

Use of "sodium phenoxide-methyl salicylate" as a catalyst in exchange esterification. K. N. KINZERSKAJA (J. Appl. Chem. Russ., 1937, 10, 1889—1893).—Benzyl salicylate is obtained in 73% yield, and the cinnamate in 40% yield, by adding NaOPh to 1 : 1 CH₂Ph·OH-*o*-OH·C₆H₄·CO₂Me or -CHPh·CH·CO₂Me mixtures, distilling off the MeOH liberated, and heating the product at 160—170°/50—80 mm., when excess of CH₂Ph·OH distils off. R. T.

α-Bromo-β-methoxy-β-phenylpropionic acids. E. J. VAN LOON and H. E. CARTER (J. Amer. Chem. Soc., 1937, 59, 2555—2557).—Contrary to Schrauth and Geller (A., 1922, i, 1125) pure CHPh·CH·CO₂H and Hg(OAc)₂ in MeOH give β-methoxy-β-phenyl-anhydro-α-hydroxymercuriropionic acid, decomp. 210—211°, but more prolonged contact gives a compound (I), decomp. 210—212°, possibly the mixed acid, OAc·[Hg·CH(CHPh·OMe)·CO₂]₂·H, insol. in CHCl₃. The Hg compounds absorb 2 Br, but give mixtures under all conditions. The best method is to add Br to (I) in aq. KBr, which leads to much α-bromo-β-methoxy-β-phenylpropionic acid, m.p. 139—140° (lit. 126—127°), and a little of the form, m.p. 165—170° (182—183°), readily separated by way of the Na salts.

R. S. C.

Configuration and mobility of cyclohexene. J. BÖESEKEN and W. J. F. DE RIJCK VAN DER GRACHT (Rec. trav. chim., 1937, 56, 1203—1210).—Butadiene and maleic anhydride in C₆H₆ yield Δ¹-cyclohexene-4 : 5-dicarboxylic anhydride, which is hydrolysed (H₂O) to the acid (I); similarly from isoprene, 1-methyl-Δ¹-cyclohexene-4 : 5-dicarboxylic anhydride, m.p. 63—64° [acid (II), m.p. 147—148°], is prepared, and from βγ-dimethyl-Δ^α-butadiene, 1 : 2-dimethyl-Δ¹-cyclohexene-4 : 5-dicarboxylic anhydride, m.p. 78—79° [acid (III), m.p. 204°]. (II), which contains an asymmetric C, is resolved through its strychnine salt, m.p. 167°, into two isomerides, both m.p. 147—148°, [α]_D²⁰ ±16.5° in EtOH, but (I) and (III) cannot be resolved, indicating that the mobilities of these acids are too great to allow the existence of stable isomerides.

J. D. R.

Condensation of acetone with phenylpyruvic acid. P. CORDIER (Compt. rend., 1937, 205, 918—920; cf. A., 1912, i, 770).—Prolonged interaction of CH₂Ph·CO·CO₂Na (1 mol.) with COMe₂ (5 mols.) and K₂CO₃ (1 mol.) (KOH gives a smaller yield) at room temp. affords α-hydroxy-γ-keto-α-benzylvaleric acid, m.p. 105°, which with HCl-AcOH affords an unsaturated acid, m.p. 93°.

J. L. D.

Condensation of ethyl tartrate with cyclic ketones and the molecular rotation of the resulting compounds. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1937, 12, 487—492).—Et₂ *d*-tartrate is readily condensed with the appropriate cyclic ketone by P₂O₅ at 80—90° to the following Et₂ *d*-dioxysuccinates : -cyclopentylidene-, b.p. 170—171°/12 mm., [α]_D²⁰ -40.55; -cyclohexylidene-, b.p. 178°/12 mm., [α]_D²⁰ -35.37°; -*o*-methylcyclohexylidene-, b.p. 184°/14 mm., [α]_D²⁰ -21.81°; -*m*-methylcyclohexylidene-, b.p. 180°/14 mm., [α]_D²⁰ -35.42°; -*p*-methylcyclohexylidene-, b.p. 188°/14 mm., [α]_D²⁰ -30.49°. The mol. rotation of these homologous compounds decreases as the parachor of the ketone residue in the condensation product increases but the influence of the position of the substituent is noticed; the substitution of Me in the *o*-position is the most effective and that of the *m*-position is nearly ineffective.

H. W.

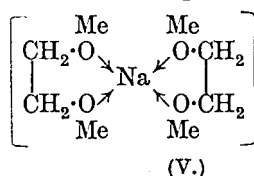
Preparation of 1 : 2-dicarboxyl chlorides by the action of chlorine on thioanhydrides. E. OTT, A. LANGENOHL, and W. ZERWECK (Ber., 1937, 70, [B], 2360—2362).—The frequent failure of PCl₅ to convert acid anhydrides into 1 : 2-dicarboxyl

chlorides is attributed to the slight difference in the affinity of P towards Cl and O. Interaction between Cl_2 and the thioanhydride is more successful since the affinity of Cl for S is sufficient to overcome the union of S and the two C and to remove S as S_2Cl_2 leaving the dichloride. Thus $o\text{-C}_6\text{H}_4(\text{COCl})_2$ is obtained in good yield by passing dry Cl_2 through thiophthalic anhydride at 245° . Similarly, pyromellitic anhydride and Na_2S afford *thiopyromellitic anhydride*, m.p. 239° , transformed by Cl_2 at 245° into pyromellityl chloride in 96% yield; this could not be isomerised by AlCl_3 at 150° .
H. W.

Chemiluminescence of phthalhydrazide derivatives. C. N. ZELLNER and G. DOUGHERTY (J. Amer. Chem. Soc., 1937, 59, 2580—2583).—The luminescence of 3- and 4-amidophthalhydrazides during oxidation is measured by a photronic cell and galvanometer. The intensity varies greatly according to the substituent and its position. The rate of oxidation (measured by the evolution of N_2) also varies, but bears no relation to the intensity of luminescence, except for compounds substituted in the heterocyclic ring. Luminescence depends on transference of energy from a decomposing enolic or dienolic mol. to unchanged diketonic mols. 3-Acet-, m.p. 160° , 3-, m.p. 269° , and 4-benz-amidophthalhydrazide, m.p. $273\text{--}274^\circ$, were prepared from the substituted Et phthalates or phthalic anhydride. $\text{NHMe}\cdot\text{NH}_2$ and $\text{NHAc}\cdot\text{C}_6\text{H}_3(\text{CO})_2\text{O}$ give α -, m.p. 302° (Ac derivative, m.p. $198\text{--}199^\circ$), and β -3-, m.p. $273\text{--}274^\circ$, and α -, m.p. 329° , and β -4-acetamido-N-methylphthalhydrazide (impure), m.p. about 260° . $(\text{NHMe})_2$ and 4:1:2-OH-C₆H₃(CO₂H)₂ give 4-hydroxy-NN'-dimethylphthalhydrazide, m.p. about 290° . o-Methylaminobenzhydrazide has m.p. $146\text{--}147^\circ$. Impure 3-hydroxy- and -chloro-phthalhydrazides were also prepared. M.p. are corr.
R. S. C.

Addition of alkali metals to phenanthrene. A. JEANES and R. ADAMS (J. Amer. Chem. Soc., 1937, 59, 2608—2622).—Contrary to Schlenck and Bergmann (A., 1928, 1031), Li adds to phenanthrene (I) in the 9:10-positions; reaction is best in $(\text{CH}_2\cdot\text{OMe})_2$ and treatment with CO_2 gives trans-9:10-dihydrophenanthrene-9:10-dicarboxylic acid (II), m.p. $235\text{--}242^\circ$ (decomp.). The product obtained by EtOH from the Li_2 compound is 9:10-dihydrophenanthrene; it yields 1:2:3:4-tetrahydrophenanthrene, when hydrogenated, by rearrangement of the 1:4:9:10- H_4 -compound initially formed. In $(\text{CH}_2\cdot\text{OMe})_2$ K reacts readily with (I), Na less rapidly but also smoothly. Carbonation yields (II), but, unless the (I) was freed from fluorene, some fluorene-9-carboxylic acid, dimorphic, m.p. 226° or 232° (decomp.) (*Me* ester, m.p. $67\text{--}68^\circ$), is formed, particularly under conditions expected to favour reaction of an impurity present in small amount. The last-mentioned acid is the product termed 9:9':10:10'-tetrahydro-9:9'-diphenanthryl-10:10'-dicarboxylic acid by Schlenck. Smooth dehydrogenation of (II) cannot be effected; $\text{K}_2\text{Fe}(\text{CN})_6$ causes also loss of CO_2 and gives phenanthrene-9-carboxylic acid; CrO_3 gives phenanthrenequinone. Methylation of (II) gives the *Me*₂ ester, m.p. 128° ; heating with Ac_2O affords cis-9:10-dihydrophenanthrene-9:10-dicarboxylic an-

hydride (III), m.p. $193\text{--}5^\circ$, and a little phenanthrene-9:10-dicarboxylic anhydride (IV), m.p. 322° ; heating alone gives a little (IV) and much cis-9:10-dihydrophenanthrene-9:10-dicarboxylic acid, double m.p. 196° and 232° (*Me*₂ ester, m.p. 119°). This *cis*-acid is unstable; it dissolves in NaOH to an orange solution (containing either the enolic or dienolic form), which soon becomes colourless and then yields the *trans*-acid (II), which is also obtained from the *cis*-acid in hot AcOH; at $230\text{--}240^\circ$ alone or with CrO_3 in cold AcOH it loses H_2 and gives (IV); it is obtained from the anhydride (III). The anhydride (IV) is extremely stable; analogies are discussed and the stability is considered to be due to proximity of the two CO_2H of the corresponding acid owing to (a) alteration of the valency angles by the α -substituents (the two Ph rings) and (b) the shortening of 9:10-C-C linking by the unusually aliphatic nature of this linking. The acid corresponding with (IV) cannot be prepared; dissolution in hot NaOH (cold NaOH is without effect), followed by acidification, regenerates the anhydride, but NaOH- Me_2SO_4 gives *Me*₂ phenanthrene-9:10-dicarboxylate, m.p. 131° ; $\text{MeOH}\cdot\text{H}_2\text{SO}_4$ is without effect on (III). Reaction of alkali metals with (I) is believed to produce equilibrium with the 9-ion and 9:10-di-ion, probably in solvated form, the existence of which is indicated by temporary disappearance of the colour on too rapid addition of CO_2 ; some of the solvent $(\text{CH}_2\cdot\text{OMe})_2$ is removed from the reaction sphere, probably as the solvate (V),



formation of which would account for the advantage of using $(\text{CH}_2\cdot\text{OMe})_2$ as solvent. The anhydride (IV) undergoes reactions of $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$. Thus with PhMe and AlCl_3 it gives 9-p-toluoyl-10-phenanthroic acid, m.p. 236° (softens at 231°), and ditolylphenanthroic acid, m.p. 247° . With C_6H_6 and AlCl_3 it gives 9-benzoyl-10-phenanthroic acid, m.p. 232° , converted with difficulty (10—15%) by P_2O_5 at $220\text{--}260^\circ$ into 1:2:3:4-dibenzanthraquinone and by BzCl in $\text{C}_6\text{H}_3\text{Cl}_3$ into a keto-lactone, $\text{C}_{22}\text{H}_{14}\text{O}_3$, m.p. 228° , reconverted into the parent acid by KOH. With $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (IV) gives the product, $\text{C}_{22}\text{H}_{12}\text{ON}_2$, m.p. 279° ; (III) gives the product, $\text{C}_{22}\text{H}_{14}\text{ON}_2$, m.p. 274° .
R. S. C.

Synthesis of conjugated bile acids. IV. Bodi and Mueller procedure. F. CORTESE (J. Amer. Chem. Soc., 1937, 59, 2532—2534; cf. A., 1937, II, 342).—Prep. of Et and Me cholate, Et deoxycholate, cholyl- and deoxycholyl-hydrazide and -azide, Na tauro- and taurodeoxycholate, and glyco- and deoxyglyco-cholic acid and their Na salts in good yields is described.
R. S. C.

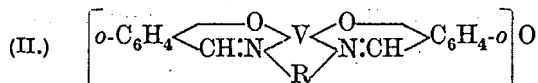
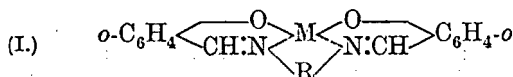
Preparation of esters of dihydronaphthalenedicarboxylic acids.—See B., 1937, 1314.

Manufacture of polycyclic aromatic aldehydes and carboxylic acids.—See B., 1937, 1315.

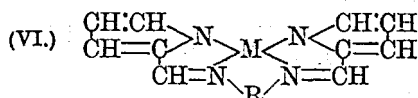
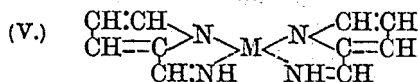
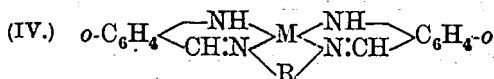
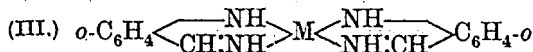
Preparation of m-dimethylaminobenzaldehyde. I. A. C. BOTTOMLEY, W. COCKER, and (Miss) P. NANNEY (J.C.S., 1937, 1891—1892).—Interaction of $m\text{-CHO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ and $\text{CH}(\text{OEt})_3$ in

5% HCl-EtOH yields m -(OEt) $_2$ CH·C $_6$ H $_4$ ·NH $_2$, methylated (MeI-Na $_2$ CO $_3$) to m -dimethylaminobenzaldehyde methiodide, m.p. 185—186° (decomp.), which, when heated at 150—160°/10—15 mm., is converted into m -dimethylaminobenzaldehyde, b.p. 137.5—138°/9 mm. [oxime, m.p. 75—76°; semicarbazone, m.p. 218—222° (slow heating) or 228—229° (instantaneous); picrate, m.p. 147—147.5°]. J. D. R.

Internal complex salts of the aldimine and azo-series. P. PFEIFFER, T. HESSE, H. PFITZNER, W. SCHOLL, and H. THIELERT with, in part, LÜBBE (J. pr. Chem., 1937, [ii], 149, 217—296).—Metal-organic complexes of many new types are described. They exhibit the colours and solubility in org. solvents characteristic of the class. Substances of type (I) (M = Cu, Ni, or Zn) are obtained from the metal acetate and (a) o -hydroxy-aldehyde and diamine or (b) the preformed di- o -hydroxyarylidenediamine; they are in general stable to 2N-NaOH and H $_2$ SO $_4$ at room temp. Substances of type (II) are obtained

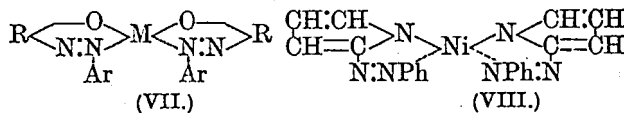


from VO·OAc and the Schiff's base in hot C $_5$ H $_5$ N or EtOH; O in these compounds can be replaced by 2 Cl or 2 OAc, which are ionic; except for compounds derived from o -OH·C $_6$ H $_4$ ·COMe, they are very stable, some even being only slowly decomposed by cone. H $_2$ SO $_4$. The VO compounds are obtained from the corresponding Fe or Mg compounds by VO·OAc in C $_5$ H $_5$ N, which confirms Treibs' view that the naturally occurring VO-porphyrins are secondary products derived from the Fe or Mg derivatives; however, Cu(OAc) $_2$ gives the Cu compounds from the VO derivatives, and the reverse replacement does not occur. Schiff's bases and UO $_2$ (OAc) $_2$ give good yields of UO $_2$ -complexes [(I) M = UO $_2$], which are not stable, being decomposed by cold acid or warm alkali. Cu and Ni salts with o -aminoarylideneamines give very readily substances of types (III) and (IV) (M = Cu or Ni); pyrrole-2-methyleneimine or amines give similarly substances (V) and (VI) (M = Cu or Ni);



these resemble (I) in properties. Hydroxyazo-compounds readily form substances (VII) (M = Ni or Cu). The Cu compound [(VII) R = OH·C $_6$ H $_3$; Ar = Ph] from benzeneazoresorcinol is so stable to alkali that it is convertible into a *Me* $_2$ ether and Bz $_2$

derivative, +0.5C $_5$ H $_5$ N, which with dil. HCl give 2:4-OH·C $_6$ H $_3$ (OH)·N:NPh and 2-hydroxy-4-benzoyloxy-

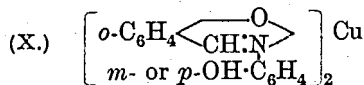


azobenzene, m.p. 139°, respectively; the Ni compounds of this series are less stable. A Cu compound (VII) containing SO $_3$ H in R is also obtained. 2-Pyrroleazobenzene, m.p. 62°, gives the Ni compound (VIII). No internal complexes are formed from m - or p -compounds, and some o -compounds do not react; in certain cases complexes formed are not of the type mentioned.

Aldimines and ketimines described below are prepared from the aldehyde and base in EtOH or the hydrochloride of the base and NaOAc in EtOH. Salicylald- o -hydroxyphenylimine, m.p. 181°, gives the

Cu derivative (IX), Cu $\begin{array}{c} \diagup \text{O-C}_6\text{H}_4 \diagdown \\ \text{O-C}_6\text{H}_4\text{-CH} \end{array}$ N, m.p. about

390°, anhyd., +PhNO $_2$, +C $_5$ H $_5$ N, and +NH $_3$ ·0.5H $_2$ O, but salicylald- m -, m.p. 130°, and - p -hydroxyphenylimine, m.p. 135°, give only the "bimol." Cu derivative (X); the Cu derivative, anhyd. and +2MeOH,



of the p -compound is stable to 1% KOH, but not to mineral acid, and with BzCl and 0.2N-KOH gives p -NHBz·C $_6$ H $_4$ ·OBz. The analogous Cu derivative, +C $_6$ H $_6$ and anhyd., from resorcyldiphenylimine, m.p. 131°, is much less stable to alkali.

NH $_2$ ·CHMe·CH $_2$ ·NH $_2$ ·2HCl, m -OH·C $_6$ H $_4$ ·CHO, Cu(OAc) $_2$, and NaOAc in aq. EtOH give the Cu derivative, +1.5H $_2$ O, of type (I) (R = ·CH $_2$ ·CHMe·). Other Cu derivatives of type (I) are obtained from disalicylald-4-chloro-, -4-nitro-, and -4-carboxy-1:2-phenylenedi-imide, m.p. indef., and disalicylald-naphthylene-1:8-di-imide; the Cu derivative of o -OH·C $_6$ H $_4$ ·CHO (XI) with (NH $_2$ ·CHPh) $_2$ and NaOAc in EtOH gives a Cu derivative {(I) R = [CHPh] $_2$ }, anhyd. and +CHCl $_3$, whilst 4:1:8-SO $_3$ H·C $_6$ H $_5$ (NH $_2$) $_2$ affords the Ba, Pb, and unstable NH $_4$ salts of a similar Cu derivative. Ni derivatives are obtained analogous to (IX) and (X) (p -compound only prepared), and the methods indicated above afford Ni derivatives (I), in which R = ·CHMe·CH $_2$ · (XII), 4:1:2-C $_6$ H $_3$ Cl<, 4:1:2-NO $_2$ ·C $_6$ H $_3$ <, and 1:8-C $_6$ H $_6$ <; that in which R = [CHPh] $_2$ is obtained anhyd. and +CHCl $_3$. The Ni derivative of (XI) and 1:3:4-CO $_2$ H·C $_6$ H $_3$ (NH $_2$) $_2$ in EtOH yield a Ni derivative [(I) R = 4:1:2-CO $_2$ H·C $_6$ H $_3$ <] [C $_5$ H $_5$ N (loses 0.5C $_5$ H $_5$ N at 140°), NH $_4$, +2.5H $_2$ O, and conine salts; *l*-menthyl ester, +C $_5$ H $_5$ N and 0.5C $_5$ H $_5$ N; no resolution occurs], which with NH $_2$ ·CHMe·CH $_2$ ·NH $_2$ exchanges the basic component to give (XII). A Zn derivative {(I) R = [CH $_2$] $_2$ }, anhyd., +C $_5$ H $_5$ N, and +0.5(CH $_2$ ·NH $_2$) $_2$, is obtained from (XI), Zn(OAc) $_2$, NaOAc, and (CH $_2$ ·NH $_2$) $_2$ ·2HCl. (XI) and the appropriate diamine give UO $_2$ derivatives (I), in which R = [CH $_2$] $_2$, anhyd., +MeOH, and +C $_5$ H $_5$ N (mol. wt. determined in acridine), stable to cold

KOH, but not to hot KOH or cold, conc. H_2SO_4 , and $\cdot\text{CHMe}\cdot\text{CH}_2\cdot$, anhyd., +EtOH, and + $\text{C}_5\text{H}_5\text{N}$. *Disalicylaldtrimethylenedi-imide*, m.p. 163°, gives a UO_2 derivative (I), anhyd. and +MeOH; its VO derivative [(II) $\text{R} = o\text{-C}_6\text{H}_4$], anhyd., +MeOH, +AcOH, and + $\text{C}_5\text{H}_5\text{N}$ (mol. wt. determined in acridine), is very stable to H_2SO_4 and yields the corresponding dichloride and diacetate. *Di-2-hydroxy-1-naphthaldehylthylenedi-imide*, m.p. 311°, gives a UO_2 , anhyd. and +MeOH, and VO derivative [as (II); $\text{R} = [\text{CH}_2]_2$, but 1:2- $\text{CH}\cdot\text{C}_{10}\text{H}_6\cdot\text{O}$ instead of $\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{O}$]. *Di-2-hydroxy-1-naphthaldehyl- $\alpha\beta$ -diphenylethylenedi-imide*, m.p. 223°, give UO_2 and VO, anhyd. and +PhMe, derivatives.

Di-2-hydroxy-1-naphthaldehyl-o-phenylenedi-imide, m.p. 163°, gives UO_2 , anhyd. and +MeOH, and VO derivatives. *Di-o-hydroxyacetophenone-ethylenedi-imide* gives UO_2 , anhyd., +EtOH, and + $\text{C}_5\text{H}_5\text{N}$, and VO derivatives, and similar UO_2 and VO derivatives, anhyd., are obtained from *di-o-hydroxyacetophenone-o-phenylene-* (XIII) and *- $\alpha\beta$ -diphenylethylene-di-imide* (XIV), m.p. 221°, respectively. UO_2 derivatives could not be prepared from *disalicylald-tetramethylene-*, m.p. 91°, *-pentamethylene-*, m.p. 64°, or *-m-phenylene-di-imide*, m.p. 109°, *disalicylald-benzidide*, m.p. 256°, or *-stilbene-4:4'-di-imide*, m.p. 266°, (XIV), *diresorcylald-*, m.p. indef., or *diresacetophenone-ethylenedi-imide*; most of these and (XIII) failed to yield also VO derivatives. The appropriate Schiff's bases yield VO derivatives (II), in which $\text{R} = [\text{CH}_2]_2$, anhyd., + CHCl_3 , and + $\text{C}_5\text{H}_5\text{N}$ (mol. wt. determined in CHCl_3 and acridine), $\cdot\text{CHMe}\cdot\text{CH}_2\cdot$, anhyd., +MeOH, and + $\text{C}_5\text{H}_5\text{N}$, and $[\text{CHPh}]_2$; the VO derivative, anhyd. and + $\text{C}_5\text{H}_5\text{N}$, from *diresorcylaldethylenedi-imide* is decomposed by cold 10% KOH, but with Ac_2O gives the Ac_2 derivative. The following are prepared: $\text{Na}_2\text{NN}'$ -*disalicylald-stilbene-4:4'-di-imide-2:2'-disulphonate*, anhyd. and +EtOH; *2:2'-dihydroxydiphenylene-5:5'-*, m.p. 246°, and *-3:3'-diamine*, unstable; *disalicylald-2:2'-dihydroxydiphenylene-5:5'-*, m.p. 241°, and *-3:3'-di-imide*, m.p. 232°, neither of which gives a Cu complex. The prep. of $\alpha\beta$ -diphenylethylenediamine from ($\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$) $_2$ is improved.

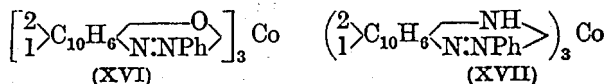
$o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (XV), m.p. 40°, with CuSO_4 or NiSO_4 in aq. NH_3 gives the Cu and Ni complexes (III). The Ni and Cu complexes [(IV); $\text{R} = o\text{-C}_6\text{H}_4$] are similarly obtained from the crude oily Schiff's base from (XV) and $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$; the Ni derivative [(IV); $\text{R} = [\text{CH}_2]_2$] is also prepared from a crude condensation product, but the Cu analogue is prepared from *di-o-aminobenzaldethylenedi-imide* (prep. at room temp. without a condensing agent), m.p. 178° (Ac_2 derivative, m.p. 200°). *Di-o-aminobenzald-p-phenylene-*, m.p. 215° (decomp.), and *-diphenylene-4:4'-di-imide*, m.p. 273—274°, are prepared by use of dil. NaOH; neither gives a Cu complex.

The Cu and Ni complexes (V) are obtained from pyrrole-2-aldehyde and CuSO_4 or NiSO_4 in aq. NH_3 . The Cu and Ni complexes [(VI); $\text{R} = o\text{-C}_6\text{H}_4$] were similarly obtained from the aldehyde and $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in H_2O , but the Cu and Ni derivatives [(VI); $\text{R} = [\text{CH}_2]_2$] are prepared from *di(pyrrole-2-ald)ethylenedi-imide*, m.p. about 175° (decomp.). *Di(pyrrole-2-ald)-diphenylene-4:4'-di-imide*, m.p. about 270° (decomp.), gives a Cu derivative [(VI); $\text{R} = \cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot$], but

di(pyrrole-2-ald)-p-phenylenedi-imide, m.p. 210—212° (decomp.), gives no complex salts.

Benzeneazo-*p*-cresol, m.p. 104°, gives a Cu derivative [(VII); $\text{Ar} = \text{Ph}$, $\text{R} = 4\text{-C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{O-1} \\ \text{N-2} \end{smallmatrix}$], but *m*- (prep. from the OMe compound by AlBr_3) and *p*-hydroxyazobenzene do not react with CuSO_4 . $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NPh}$, m.p. 79—80°, and benzeneazoresorcinol, m.p. 170°, give Ni derivatives of type (VII). Benzeneazo-2-naphthol-4-sulphonic acid gives a Ni [(VII); $\text{Ar} = \text{Ph}$, $\text{R} = 4\text{-SO}_3\text{H}\cdot\text{C}_{10}\text{H}_5 \begin{smallmatrix} \text{O-2} \\ \text{N-1} \end{smallmatrix}$], +6 H_2O , +6 NH_3 , and +3($\text{CH}_2\cdot\text{NH}_2$) $_2$, and Cu derivative, anhyd. and +6.5 H_2O [*di(ethylenediamine)*, +3 H_2O , Cu, +2 NH_3 , K_2 , and Ba salts]. 2:2'-Dihydroxyazobenzene gives a Cu derivative [(VII) $\text{Ar} = o\text{-C}_6\text{H}_4\cdot\text{OH}$], anhyd. and + $\text{NH}_3\cdot 0.5\text{H}_2\text{O}$. 2:1-OH $\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{NPh}$ gives a Co derivative (XVI).

Benzeneazo- β -naphthylamine and $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ in $\text{NH}_3\text{-EtOH-H}_2\text{O}$ give the Co^{III} complex (XVII), but attempts to obtain Cu derivatives by $\text{CuSO}_4\text{-NH}_3$



from 6-amino-3:4'-dimethylazobenzene and benzeneazo-2-naphthylamine-4-sulphonic acid resulted in oxidation to the dimethyltriazole, 4:1:2- $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{N}\cdot\text{C}_6\text{H}_4\text{Me-}p$, m.p. 125—126°, and the phenylnaphthatriazole derivative, 1:2- $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, cryst. (Cu^{II} , anhyd. and +3 NH_3 , and Na_2 salts) (cf. Crippa, A., 1929, 181).

R. S. C.

Co-ordinated copper and nickel compounds of salicylidene derivatives. L. HUNTER and J. A. MARRIOTT (J.C.S., 1937, 2000—2003).—By interaction of the appropriate salicylidene derivative (2 mols.) with the metal acetate (1 mol.) in hot EtOH, or by interaction of salicylaldehyde (2 mols.), metal acetate (1 mol.) and amine or hydrazine derivative (2 mols.) in hot EtOH, the following derivatives

of the type $\left[\begin{smallmatrix} \text{C}_6\text{H}_4\cdot\text{O} \\ \text{CH}\cdot\text{N}\cdot\text{R} \end{smallmatrix} \right]_2 \text{M}$ (where R is Ar, NHAr,

or $\text{NH}\cdot\text{CO}\cdot\text{NH}_2$) are formed: Cu^{II} *salicylidene-o-*, m.p. 243—246° (decomp.), *-m-*, m.p. 188° (decomp.), *-p-toluidine*, m.p. 211—213° (decomp.), *- α -*, m.p. 259° (decomp.), *- β -naphthylamine*, m.p. 194—196° (decomp.), *-m-*, m.p. 210—212° (decomp.), *-p-chloroaniline*, m.p. 240°, *-p-bromoaniline*, m.p. 250—251°, *-m-*, m.p. 272° (decomp.), *-p-nitroaniline*, m.p. 313° (decomp.), *-o-*, m.p. 222° (decomp.), *-p-anisidine*, m.p. 179° (decomp.), *-hydrazone*, decomp. 270—275°, *-phenylhydrazone*, m.p. 174°, *-p-nitrophenylhydrazone*, m.p. 221° (decomp.), and Cu^{II} *salicylaldimine*, m.p. 195° (decomp.); *Ni salicylidene-aniline*, m.p. 248° (decomp.), *-o-*, m.p. 293° (decomp.), *-m-*, m.p. 260° (decomp.), *-p-toluidine*, m.p. 274° (decomp.), *- α -*, m.p. 311° (decomp.), *- β -naphthylamine*, m.p. 220° (decomp.), *-o-anisidine*, m.p. 319° (decomp.); *nickel-salicylaldimine*, m.p. 335° (decomp.), *-salicylaldazine*, stable at 360°, *-disalicylidenebenzidine*, m.p. >360°; *Ni salicylidene-hydrazone*, decomp. 313°, *-phenyl-*

hydrazone, decomp. about 230°, and -semicarbazone, decomp. 302°. None of the Cu derivatives offers any advantage over that of salicylaldoxime for the determination of Cu.

J. D. R.

Addition of ketens to hydrocarbons. E. H. FARMER and M. O. FAROOQ (Chem. and Ind., 1937, 1079—1080).— CPh_2CO appears to react successfully with all simple conjugated dienic hydrocarbons, whether cyclic or open-chain, since it gives homogeneous cryst. additive products with cyclopentadiene, cyclohexene (I), cyclohexadiene (II), $\beta\gamma$ -dimethylbutadiene, and piperylene. It does not appear to react with CMe_2CMe_2 . The H_2 -derivative of the additive product from (II) is identical with the additive product (III) from (I) so that in these cases addition cannot involve the formation of a six-C ring. Further the product of the hydrolytic fission of (III) does not correspond with the diphenylcyclohexylacetic acid of Ziegler and Schnell (A., 1924, i, 850) so that Staudinger's simple explanation of the change, $\text{CH}_2\text{CH}_2\text{CH}(\text{CPh}_2)\text{CH}_2\text{CO} \rightarrow \text{C}_6\text{H}_{11}\text{CPh}_2\text{CO}_2\text{H}$, is inadequate. The behaviour of the various additive products towards hot alkali is not uniform but, where fission occurs at all, more than one product results.

H. W.

Action of ω -bromoacetophenone on dimagnesium acetylenyl dibromide. S. A. ZABOEV (J. Gen. Chem. Russ., 1937, 7, 1858—1859).— $(\text{:C-MgBr})_2$ and COPhCH_2Br in Et_2O yield $\alpha\zeta$ -dibromo- $\beta\epsilon$ -diphenyl- Δ^7 -hexene- $\beta\epsilon$ -diol, m.p. 121—123°. R. T.

Lability of the dimethylamino-group in some dimethylaminoketones. (MISS) A. JACOB and J. MADINAVEITIA (J.C.S., 1937, 1929—1931).—Treatment of $\text{CH}_2\text{Bz}\cdot\text{NMe}_2$ (I) with MeI-KOH-MeOH yields BzOH and NMe_3 , both of which are formed from $\text{CH}_2\text{Bz}\cdot\text{NMe}_3\text{I}$ and MeOH-KOH . Similarly, treatment of $\text{Bz}\cdot[\text{CH}_2]_2\cdot\text{NMe}_2$ (II) with MeI-KOH-MeOH , or of $\text{Bz}\cdot[\text{CH}_2]_2\cdot\text{NMe}_3\text{I}$ with KOH-MeOH , yields NMe_3 and a substance, $\text{C}_{18}\text{H}_{16}\text{O}_2$, m.p. 172° (probably dibenzoylcyclobutane). From $\text{CH}_2\text{Ac}\cdot\text{NMe}_2$ (III) by treatment with MeI-KOH-MeOH , $\text{NMe}_4\cdot\text{OH}$ is formed. (I) with $\text{NHPh}\cdot\text{NH}_2$ in aq. AcOH yields the phenylosazone of BzCHO , also obtained from $\text{CH}_2\text{Bz}\cdot\text{NH}_2\cdot\text{HCl}$ and $\text{NHPh}\cdot\text{NH}_2$. Similar treatment of (II) and (III) yields 1:3-diphenyl- and 1-phenyl-3-methyl-pyrazoline, respectively. With N_2H_4 , (I) gives a substance, $\text{C}_{16}\text{H}_{16}\text{N}_6$, m.p. 206°, and (II) yields a substance, $\text{C}_6\text{H}_8\text{N}$, m.p. 141°.

J. D. R.

Constitution of Liebermann's benzanthrone. E. GHIGI (Ber., 1937, 70, [B], 2469—2478).—Liebermann's compound is identified as 2:3-dimethylbenzanthrone (I). Its amended prep. by the action of conc. H_2SO_4 on *ms*-isoamyloxanthranol is described. Alkaline oxidation of (I) does not proceed satisfactorily and the compound is therefore reduced by Zn and conc. HCl in AcOH to 9-hydroxy-2:3-dimethyl-1:9-trimethylenephenanthrene, m.p. 176°. This is oxidised by KMnO_4 in presence of NaOH to 3:4-dimethyldiphenyl-5:2'-dicarboxylic-6-glyoxylic acid (II), m.p. 260—262° (decomp.) after changing at 250°, which is converted by KMnO_4 in acid solution into 3:4-dimethyldiphenyl-5:6:2'-tricarboxylic acid (III), m.p.

239—240°. This is decarboxylated in boiling quinoline containing Cu to 3:4-dimethyldiphenyl (IV), b.p. 281—283°, characterised by its oxidation to diphenyl-3:4-dicarboxylic acid, m.p. 201—202° (anhydride, m.p. 140—141° when rapidly heated); a dimethyldiphenyldicarboxylic anhydride, m.p. 190—191°, is obtained as by-product and is transformed by conc. H_2SO_4 at 150—160° into a sulphonated fluorenonecarboxylic acid. Oxidation of (II) in acid solution gives 4-methyldiphenyl-3:5:6:2'-tetracarboxylic acid, m.p. 335° after incipient blackening at 300°, decarboxylated to 4-methyldiphenyl, m.p. 47—48°. Treatment of (II) or (III) with conc. H_2SO_4 at 150—160° yields 2:3-dimethylfluorenone-1:5-dicarboxylic acid, m.p. 320° after softening at 290°. Distillation of (II) with Ca(OH)_2 affords a dimethylfluorene, m.p. 107—108° [with a small proportion of (IV)], which is oxidised to a methylfluorenonecarboxylic acid, m.p. 291—292°, and a dimethylfluorenone, m.p. 101—102°.

H. W.

Compounds of the benzanthrone series.—See B., 1937, 1315.

Condensation of aldol with dimedon. I. KASUYA (J. Amer. Chem. Soc., 1937, 59, 2742).—Dimedon and aldol give the product (I), $\text{C}_{20}\text{H}_{30}\text{O}_5$, m.p. 146—148°, and crotonaldehyde gives the product (II), $\text{C}_{20}\text{H}_{28}\text{O}_4 + 0.5\text{EtOH}$, m.p. 185—186°. Fricke's substance, m.p. 170—172° (A., 1922, i, 300), supposed to be (I), was probably impure (II), since his conditions allow dehydration of aldol.

R. S. C.

Acylation of diazomethane. II. Reaction of diazomethane with *O*-acetylmandelyl chloride and some transformations of the product. W. BRADLEY and J. K. EATON (J.C.S., 1937, 1913—1915).—Acetylmandelyl chloride with CH_2N_2 in Et_2O yields α -acetoxybenzyl chloromethyl ketone, m.p. 57° (hydrolysed by NaOAc to AcBz , which is also formed by spontaneous decomp. on long keeping), and hydrolysed by aq. H_2SO_4 to benzylglyoxal (dioxime, m.p. 163°).

J. D. R.

Reaction between hydrazoic acid and benzil. M. A. SPIELMAN and F. L. AUSTIN (J. Amer. Chem. Soc., 1937, 59, 2658—2660).— Bz_2 , NH_3 , and H_2SO_4 in CHCl_3 give mainly $\text{NHBz}\cdot\text{CO}\cdot\text{NHPh}$, some $(\text{CO}\cdot\text{NHPh})_2$, and small amounts of BzOH , NH_2Ph , 5-amino-, 5-anilino-, and 5-benzamido-1-phenyl-tetrazole. Benzil- γ -dioxime is unaffected by $\text{HN}_3\cdot\text{H}_2\text{SO}_4$ and is thus not an intermediate. $\text{NHBz}\cdot\text{CO}\cdot\text{NHPh}$ is also unattacked and is thus not the forerunner of the tetrazoles, which are formed by an independent, but obscure, mechanism. HN_3 is stable in $\text{H}_2\text{SO}_4\text{-CHCl}_3$ and $>\text{NH}$ is thus not the effective reagent.

R. S. C.

Preparation of diphenacyl. T. AJELLO (Gazzetta, 1937, 67, 708—710).— $(\text{CH}_2\text{Bz})_2$ (I) is prepared cheaply from CH_2BzBr in 95% EtOH , which with aq. KOH gives a 95% yield of $\text{CHBzBr}\cdot\text{CH}_2\text{Bz}$, converted by Mg and EtOH into (I).

E. W. W.

3-epiHydroxyætiolchoyl isohexyl ketone. M. I. USCHAROV, P. F. EPIFANSKI, and A. D. TSCHINAËVA (J. Gen. Chem. Russ., 1937, 7, 1825—1827).—Oxidation according to Ruzicka (A., 1934, 1221) of epicholestanyl acetate yields, apart from androsterone

acetate, 3-epihydroxycatioallocholyl isohexyl ketone, m.p. 175—177° (acetate, m.p. 135—136°), the semicarbazone, m.p. 223—227° (decomp.), of which separates when the neutral fraction of the oxidation products is allowed to react with semicarbazide during 20 days.

R. T.

Dehydroandrosterone oxide. M. I. USCHAKOV and A. I. LUTENBERG (J. Gen. Chem. Russ., 1937, 7, 1821—1824).—Dehydroandrosterone (I) and BzO_2H in CHCl_3 yield the 5 : 6-oxide of (I), m.p. 227.5°, converted by dil. H_2SO_4 into androstane-3 : 5 : 6-triol-17-one. This is oxidised (CrO_3 in AcOH) to androstan-5-ol-3 : 6 : 17-trione, a CHCl_3 solution of which is treated with dry HCl at 0°, to yield Δ^4 -androstene-3 : 6 : 17-trione.

R. T.

Polyphenyl derivatives of oo'-ditolyl. III. Condensation of phenol with phenanthrenequinone. **IV.** Transformations of di-*p*-hydroxyphenylphenanthrone. P. G. SERGEEV (J. Gen. Chem. Russ., 1937, 7, 1645—1653, 1654—1660).—III. Bachmann's work on the prep. and rearrangement of 9 : 10-dianisylidihydrophenanthrenediol (A., 1932, 745) is confirmed. 9 : 9-Di-*p*-anisylphenanthrone (I) and KOH in EtOH at 150° (4 hr.) yield 2-(di-*p*-anisylmethyl)diphenyl-2'-carboxylic acid, m.p. 136—137°, which regenerates (I) when heated at the m.p. (I) is also synthesised from $\text{C}_6\text{H}_4 > \text{C}(\text{OH})\cdot\text{CO}_2\text{Me}$ and

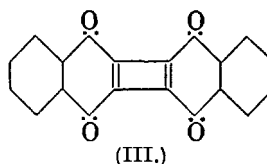
p- $\text{OMe}\cdot\text{C}_6\text{H}_4\text{MgBr}$, or from 9 : 9-dichlorophenanthrone and anisole. Phenanthrenequinone and PhOH in $\text{HCl}\text{--EtOH}$ at room temp. (3 hr.) yield 9 : 9-di-(*p*-hydroxyphenyl)phenanthrone (II), m.p. 255—256° (+ H_2O , m.p. 244—246°; Ac_2 derivative, m.p. 216—217°), from which (I) is prepared by methylation, and its Et_2 analogue, m.p. 139—140°, by ethylation.

IV. (II) and Zn in boiling 20% NaOH yield 10-hydroxy-9 : 9-di-*p*-hydroxyphenyl-9 : 10-dihydrophenanthrene (III), m.p. 204—205° (+ C_6H_6 , m.p. 132—135°; Me_2 ether, m.p. 171—172°; Ac_2 ester, + MeOH , m.p. 248—249°), which is oxidised by AgOH to 2-(hydroxydi-*p*-hydroxyphenylmethyl)diphenyl-2'-carboxylic acid. (III) gives 9 : 10-di-*p*-hydroxyphenylphenanthrene (IV), m.p. 302—303° (Ac_2 ester, m.p. 282°), when treated with HBr in AcOH at room temp. (IV) is also prepared by distilling (I) from Zn dust.

R. T.

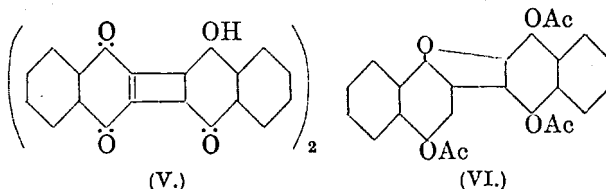
Processes of polymerisation. Condensation of 1 : 4-naphthaquinone to 2 : 3-dinaphthylenediquinone by pyridine in two stages. E. ROSENHAUER, F. BRAUN, R. PUMMERER, and G. RIEGELBAUER (Ber., 1937, 70, [B], 2281—2295).—Passage of air through a boiling solution of β -naphthaquinone in EtOH containing AcOH and quinoline followed by oxidation of the quinhydrone with PbO_2 in $\text{C}_6\text{H}_3\text{Cl}_3$ gives 1 : 1'-dinaphthyl-3 : 4 : 3' : 4'-diquinone, m.p. 288—290° (also + PhNO_2). Similarly air transforms α -naphthaquinone (I) in AcOH containing $\text{C}_6\text{H}_5\text{N}$ at 40—45° into a quinhydrone, oxidised to 2 : 2'-dinaphthyl-1 : 4 : 1' : 4'-diquinone (II), decomp. 274—275° (block), which with 1 : 4 : 1' : 4'-tetrahydroxy-2 : 2'-dinaphthyl yields a black-violet quinhydrone, decomp. >200° after darkening, of unexplained structure. 1 : 4 : 1' : 4'-Tetra-acetoxy-2 : 2'-

dinaphthyl has m.p. 227°. 2 : 3-2' : 3'-Dinaphthylene-



(III.)

1 : 4 : 1' : 4'-diquinone (III), m.p. >400°, is obtained by treating (I) with boiling $\text{C}_6\text{H}_5\text{N}$, with $\text{C}_6\text{H}_5\text{N}$ in AcOH at 100° followed by boiling PhNO_2 , with AcOH and $\text{C}_6\text{H}_5\text{N}$ in PhNO_2 at 145°, or from (II) and boiling $\text{C}_6\text{H}_5\text{N}$. It is transformed by cautious distillation with Zn dust into 2 : 3-2' : 3'-dinaphthylene, m.p. $365^\circ \pm 2^\circ$ after darkening at 310° and softening at 362—363°, which gives a very unstable picrate, $(\text{C}_{20}\text{H}_{12})_3[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}]_2$, m.p. >260°. Addition of Zn dust to a solution of (IV) in boiling $\text{C}_6\text{H}_5\text{N}$ containing Ac_2O and a little AcOH gives 1 : 4 : 1' : 4'-tetra-acetoxy-2 : 3-2' : 3'-dinaphthylene, m.p. 278—280° (decomp.). Reduction of (III) with Zn dust- AcOH , $\text{Sn}\text{--HCl}$, or H_2SO_3 is slow and incomplete whereas alkaline SnCl_2 or $\text{Na}_2\text{S}_2\text{O}_4$ and NaOH readily give 1 : 4 : 1' : 4'-tetrahydroxy-2 : 3-2' : 3'-dinaphthylene (IV), decomp. >250°. Crude (III), particularly if prepared by means of $\text{C}_6\text{H}_5\text{N}\text{--AcOH}$, contains the



(V.)

(VI.)

anhydro-quinhydrone of dinaphthylenediquinone (V), m.p. about 382° (block; decomp.), more conveniently obtained from (IV); its Ac_2 derivative has m.p. 285° (decomp.) when placed on block preheated to 280°. Reductive acetylation transforms (V) into (probably) the corresponding hexa-acetate, decomp. >300°, re-converted by 50% H_2SO_4 into (V). During the alkaline reduction of (III) a mixture of sparingly sol. K salts separates, better obtained by treatment of (III) with KOH alone in presence or absence of air. This is converted by mineral but not by org. acids into a red compound, $\text{C}_{20}\text{H}_{10}\text{O}_4$, m.p. $296^\circ \pm 2^\circ$ on Cu block preheated to 270°, transformed by reductive acetylation into the corresponding dihydrotriacetate (VI), decomp. 293° after darkening. 3 : 3'-Dihydroxy-2 : 2'-dinaphthyl-1 : 4 : 1' : 4'-diquinone, m.p. 272—275°, is formed as by-product of the fission with alkali.

H. W.

Preparation of 2-aminoanthraquinone from 2-chloroanthraquinone. N. N. VOROSHCHEV and V. P. SCHKITIN (J. Gen. Chem. Russ., 1937, 7, 2080—2086).—2-Aminoanthraquinone is obtained in 96% yield, and 98.5—99.5% pure, from 2-chloroanthraquinone and 25% aq. NH_3 (5 hr. at 210°) in presence of KClO_3 and Cu^{II} ; under the conditions of Groggins and Stirton (A., 1933, 277, 396) considerable contamination with Fe salts arising from corrosion of the autoclave takes place. Groggins' finding that impure products are obtained in presence of Cu^{II} salts is not confirmed.

R. T.

Configurations of some *p*-menthane derivatives. G. H. KEATS (J.C.S., 1937, 2003—2007).—Electrolytic reduction of *l*-menthone gives *trans*-*p*-

menthane (I), and *dl*-isomenthone yields the *cis*-isomeride, the configurations of the *p*-menthanes being based on a comparison of their physical properties with application of the Auwers-Skita rule. Hence *l*-menthol belongs to the *trans*- and *dl*-isomenthol to the *cis*-*p*-menthane series. *l*-Menthol gives the bromide, which is dehalogenated by various methods to give (I), whilst *dl*-isomenthol gives a mixture of *cis*- and *trans*-isomerides. A somewhat analogous isomerisation is observed in the conversion of the 8-hydroxy-*p*-menthanes into *p*-menthane, through the 8-chloro-*p*-menthanes, the *trans*-carbinol yielding the *trans*-hydrocarbon, and the *cis*-carbinol a mixture of *cis*- and *trans*-isomerides.

F. R. S.

Dehydrogenation of borneol. B. N. RUTOVSKI, I. P. LOSEV, and A. A. BERLIN (Prom. Org. Chim., 1937, 4, 410—416).—Borneol when dehydrogenated with dispersed Ni catalyst in PhMe (1 hr. at 210°, followed by 3 hr. at 220°) gives 92.5% camphor, in 91% yield. Better results are obtained with a continuous liquid-phase process, using 72:28 Al-Ni catalyst at 235—240°, and a 2:3 vaseline oil-PhMe solvent. The activity of this catalyst is lowered by presence of aluminates.

R. T.

Isomeride of cymene from camphor. I. A. PEARL and W. M. DEHN (Bull. Chem. Soc. Japan, 1937, 12, 493—494).—Treatment of camphor with 85% H_3PO_4 at 200° affords an isomeride of cymene, b.p. 180—182°, $[\alpha]_D^{25} +6.94^\circ$, probably 1-methyl-4-isopropenyl- $\Delta^{2,4}$ -cyclohexadiene.

H. W.

Stereochemistry of pinocampheols. T. KUWATA (J. Amer. Chem. Soc., 1937, 59, 2509—2511).—*d*- α -Pinene and $KMnO_4$ in 90% aq. $COMe_2$ give 1-hydroxypinocamphone, m.p. 35.5—36.5°, $[\alpha]_D^{25} -18.56^\circ$ in EtOH [semicarbazone, m.p. 230° (decomp.)], reduced by Na-EtOH to 1-*cis*-pinocampeol, m.p. 55—56°, b.p. 84—87°/3 mm. (acetate, b.p. 82—84°/3 mm.; naphthylurethane, m.p. 87.5—88°), which with CrO_3 gives *d*-pinocamphone, b.p. 61—64°/3 mm. (semicarbazone, m.p. 228°), converted by Na-EtOH into *d*-pinocampeol, b.p. 103—105°/13 mm., m.p. 65—66° (phenylurethane, m.p. 74—75°). *dl*-Pinene leads similarly to *dl*-hydroxypinocamphone, m.p. 38.5—39° [semicarbazone, m.p. 213—214° (decomp.)]; acetate, b.p. 104—108°/4 mm.], *dl*-*cis*-pinocampeol, b.p. 90—95°/3 mm., 214—217°/762 mm. (phenylurethane, an oil), *dl*-pinocamphone, b.p. 60—63°/3 mm. (semicarbazone, m.p. 207—209°), and *dl*-pinocampeol, b.p. 82—84°/5 mm. (phenylurethane, m.p. 95—96°).

R. S. C.

N-Substituted diamides of camphoric acid.—See B., 1938, 105.

Action of chloroacetic acid on Willstätter lignin and wood. N. I. NIKITIN and T. I. RUDNEVA (J. Appl. Chem. Russ., 1937, 10, 1915—1920).—Willstätter lignin dissolves in $CH_2Cl \cdot CO_2H$ (I) (2—3 hr. at 100—120°), to yield a chloroacetate (75% esterification), pptd. from the solution by Et_2O , and from which lignin is regenerated by the action of NH_3 in EtOH. Two thirds of the lignin content of pine sawdust is extracted by (I); the ester so obtained is hydrolysed as above, and carbohydrates are removed

by hydrolysis with 5% H_2SO_4 , when the final product is identical with lignin.

R. T.

Hydrogenation of uropterin. W. KOSCHARA (Z. physiol. Chem., 1937, 250, 161—174).—Uropterin (I) (xanthopterin; A., 1936, 882) is reversibly reduced by H_2S and org. SH groups, the mechanism differing from that of reduction by $Na_2S_2O_4$ or Na_2SO_3 which does not occur in aq. Na_2CO_3 . Data from hydrogenation followed by autoxidation indicate the composition $C_{13}H_{11}O_4N_{11}$ instead of $C_{19}H_{18}O_6N_{16}$ for (I), which contains 13.2—14.8% of $NH_2 \cdot N$.

F. O. H.

Quassin. II. Neoquassin. E. P. CLARK (J. Amer. Chem. Soc., 1937, 59, 2511—2514; cf. A., 1937, II, 297).—Neoquassin (I) (best purified by 2.5% KOH-EtOH) is shown by its reactions to be closely related to quassin (II). With dil. HCl (I) gives semidemethoxyquassin, but with HCl-EtOH gives ethoxyneoquassin, $C_{24}H_{34}O_6$, m.p. 180°, obtained similarly, together with some (I), from (II). CrO_3 oxidised (I) to isoquassin (III). Ac_2O -NaOAc converts (I) into anhydroquassin, but oxidises (III) to dehydroquassin, m.p. 256—263°.

R. S. C.

Rottlerin. K. S. NARANG, J. N. RAY, and B. S. ROY (Current Sci., 1937, 6, 156, and J.C.S., 1937, 1862—1865).—Rottlerin, new formula, $C_{27}H_{26}O_7$, with $KHCO_3$, K_2CO_3 , and Me_2SO_4 in $COMe_2$ gives a *Me*₄ ether, m.p. 144°, which (a) gives no Ac derivative, (b) with alkaline H_2O_2 gives a substance, $C_{31}H_{36}O_8$, m.p. 128° (decomp.), converted by catalytic hydrogenation into tetrahydrotrotlerin in *Me*₄ ether, m.p. 108°, also obtained by methylation of tetrahydrotrotlerin (I) (*Ac*₃ derivative, m.p. 178°), and (c) with $NaNO_2$ -AcOH yields a substance, (?) $C_{19}H_{21}O_6N$, which is catalytically hydrogenated to a substance, $C_{19}H_{23}O_6N$, m.p. 162°, and with alkali gives PhCHO. With EtOH-HCl (I) gives an Et_2O -sol. substance, m.p. 274—278°, and an Et_2O -insol. substance, $C_{20}H_{22}O_4$, m.p. 171°.

R. S. C.

Structure of gossypol. A. M. ZAMISCHLAIEVA and S. S. KRIVITSCH (J. Gen. Chem. Russ., 1937, 7, 1969—1971).—The infra-red absorption spectra (λ 1—10 μ) of gossypol in CCl_4 and Et_2O are indicative of the presence of CH_2 , Me, CO, C=C, and OH groups.

R. T.

Amanita toxins. IV. F. LYNEN and U. WIELAND (Annalen, 1937, 533, 93—117; cf. A., 1932, 785; 1933, 746; 1935, 267).—Extraction of the fresh material with MeOH and treatment of the solution with $Pb(OAc)_2$ appear to show that in addition to the thermostable *Amanita* toxin another poisonous constituent exists in the crude extract; this is destroyed by pptn. with heavy metals or by heat. From its solution the toxin is salted out by $(NH_4)_2SO_4$. Extraction of the dry material with EtOH and adsorption by Al_2O_3 leads to the separation of a rapidly acting toxin II from the known toxin, now named toxin I. Better separation is effected by fractional extraction of the aq. solution of the solid with Bu^oOH , whereby the first portions (A) contain 90% of toxin-II and 50% of toxin I, the second portions (B) contain almost only toxin I as active material, whilst the third portions and the aq. extract contain little active matter. Toxin I is pptd. quantitatively by $Hg(OAc)_2$

but loss of activity occurs when the ppt. is treated with H_2S ; improved results are not obtained by decomp. with Zn or Ca and salting out of the aq. solution. It cannot be fractionated by phosphotungstic acid. The most active samples of toxin I contain S. It gives a positive Hopkins-Cole and a negative Ehrlich reaction. The Keller coloration is dark green. The biuret and ninhydrin tests are negative. (II) is a complex substance the hydrolysate of which gives the ninhydrin reaction, indicating the presence of embedded NH_2 -acids. Previous to hydrolysis toxin I in EtOH neutralises alkali and gives a *K* and *Ba* salt insol. in EtOH. Treatment of *A* in H_2O -EtOH- Bu^oOH with Al_2O_3 leads to the separation of toxin II and toxin III which is slow in physiological action and is characterised by its *platinichloride*. Toxin II is obtained cryst. and is designated *phalloidine*. It has m.p. 280—282° (decomp.) when rapidly heated. It is probably $C_{30}H_{43}O_9N_7S$ and retains $5H_2O$ with unusual tenacity. It gives a cryst. *Ac_2* derivative, m.p. 203—205° (decomp.), and a non-cryst. *Bz* compound. It is neutral in solution, does not give sparingly sol. compounds with the usual alkaloidal precipitants, but affords a powdery ppt. with phosphotungstic acid in H_2SO_4 . CO_2H and $\cdot NH_2$ are absent. It contains 2 OH. It is hydrolysed to NH_2 -acids, among which alanine has been identified. A modified titration of the hydrolysate according to Willstätter-Waldschmidt-Leitz and a Van Slyke determination establish the presence of 3 $\cdot NH \cdot CO \cdot$. The toxins appear to be distantly related to the ergot alkaloids. H. W.

Catalytic transformation of heterocyclic compounds. VII. Conversion of tetrahydrofuran (furanidin) into pyrrolidine and thiophen. J. K. JURIEV and M. N. PROKINA (J. Gen. Chem. Russ., 1937, 7, 1868—1873).—Tetrahydrofuran gives pyrrolidine or thiophen in high yields when passed over Al_2O_3 in a stream of NH_3 or H_2S at 400°. R. T.

Aromatic character of the furan nucleus. Preparation and properties of simple 3-amino-furans. B. H. STEVENSON and J. R. JOHNSON (J. Amer. Chem. Soc., 1937, 59, 2525—2532).—Reactions of 3-amino- and -hydroxy-furans indicate that the furan ring has little aromatic character. Et 2-methyl-3-furoate and $N_2H_4 \cdot H_2O$ at 115—125° give a 90—93% yield of the *azide* (I), m.p. about 25°, and thence by H_2O quantitatively or by way of the *carbimide* (II), b.p. 40°/13 mm., *s-di-2-methyl-3-furylcarbamide* (III), m.p. 220—222°. With HCO_2H in H_2 or CH_4 (I) gives 3-formamido-2-methylfuran, m.p. 65.5—67°, converted best (80% yield) by rapid distillation in steam- CH_4 or, less well, by solid NaOH at 130—140° into 3-amino-2-methylfuran, b.p. 51—52°/4 mm., very unstable in air. The amine is also obtained impure in poor yield by distilling (III) or the crude *urethane* from (II) with NaOH. With $BzCl \cdot C_5H_5N$ it gives the known *Bz* derivative, with $CHCl_3 \cdot KOH$ it gives the *carbylamine* reaction, with hot H_2SO_4 under CH_4 an 89% yield of NH_3 , and with HNO_2 a *diazo*-solution, which with $\beta\text{-}C_{10}H_7 \cdot OH$ gives an *azo-dye*, m.p. 122—122.5°, but it does not undergo other *diazo*-reactions. $CH_2Br \cdot COMe$, $CH_2Ac \cdot CO_2Et$, and Na in C_6H_6 give 63% of

$CH_2Ac \cdot CHAc \cdot CO_2Et$, b.p. 131—133°/17—18 mm., converted in 74% yield by aq. H_2SO_4 -EtOH into Et 2 : 5-dimethyl-3-furoate, b.p. 96—100°/16 mm., which yields the *hydrazide*, m.p. 136—137°, and thence the *azide* (IV), m.p. 24—25°. With HCO_2H (IV) gives 3-formamido-2 : 5-dimethylfuran, b.p. 152—154°/11 mm., m.p. 80.5—81.5°, which, when heated with Cu or, better, distilled in steam from aq. alkali, yields 3-amino-2 : 5-dimethylfuran, b.p. 55—56°/4 mm. (*Bz* derivative, m.p. 152—152.4°, sublimes at 140°/2 mm.). This gives the *carbylamine* reaction and reacts with $PhCHO$ in aq. EtOH at -10° without elimination of H_2O to give a substance (? 3-phenyl-hydroxymethylimino-2 : 5-dimethylfuran or 2-phenyl-5 : 5'-dimethylfurano-2' : 3' : 5 : 4-tetrahydro-oxazole), m.p. 113—115°. The amine is hydrolysed by $Ba(OH)_2$ to $AcOH$ and $OH \cdot CHMe \cdot COMe$ by way of the *NH*-form, the ring-ketone, and $CH_2Ac \cdot CO \cdot CHMe \cdot OH$; with HNO_2 it gives a *diazo*-solution, which with $\beta\text{-}C_{10}H_7 \cdot OH$ gives an *azo-dye*, m.p. 108—110°, but gives no other *diazonium* reactions. Attempts to prepare 2-aminofuran from the *carbimide* gave only traces of impure base. M.p. are corr. R. S. C.

Heterocyclic compounds. V. Synthesis of 7-hydroxy-2-methyl-6-ethylchromone and its derivatives. R. D. DESAI and S. A. HAMID (Proc. Indian Acad. Sci., 1937, 6, A, 287—290).—2 : 4-Dihydroxy-5-ethylacetophenone (I), $NaOAc$, and Ac_2O give 7-acetoxy-3-acetyl-2-methyl-6-ethylchromone, m.p. 138°, hydrolysed to the 7-OH-compound, m.p. 193° (*Me ether*, m.p. 158°), which with Na_2CO_3 affords 7-hydroxy-2-methyl-6-ethylchromone (II), m.p. 204° (*Me ether*, m.p. 90°; *Ac* derivative, m.p. 99°). Hydrolysis of (II) with NaOH yields (I), but its *Me ether* similarly forms 2-hydroxy-4-methoxy-5-ethylbenzoic acid, m.p. 192° (*OMe*-derivative, m.p. 126°), also obtained by methylation of 2 : 4-dihydroxy-5-ethylbenzoic acid, m.p. 188°, prepared from 4-ethylresorcinol and $KHCO_3$. F. R. S.

Indigoid vat dyes containing fluorine.—See B., 1938, 42.

Phenoxthionine. II. Extension of the Ferrario reaction. C. M. SUTER and F. O. GREEN (J. Amer. Chem. Soc., 1937, 59, 2578—2580; cf. A., 1936, 861).—The appropriate *Ph aryl ether*, S (1 mol.), and $AlCl_3$ (0.5 mol.) at 100° give 4-, b.p. 186—187° (*dioxide*, m.p. 141—142°), 3- (? 1-), m.p. 83—84° (*dioxide*, m.p. 138—139°), and 2-methyl-, m.p. 38—39° (*dioxide*, m.p. 134—135°), 4-, b.p. 192—193°/7 mm. (*dioxide*, m.p. 148—149°), 3- (? 1-), m.p. 59—60° (*dioxide*, m.p. 152—153°), and 2-chloro-phenoxthionine, m.p. 88—89° (*dioxide*, m.p. 158—159°). 2-Bromophenoxthionine, $PhOH$, and Cu in $PhOH$ at 185—195° give 2-phenoxthionine, m.p. 81—82°, b.p. 230—235°/7 mm. (*dioxide*, m.p. 112—113°), which with S and $AlCl_3$ at 40° gives H_2S slowly and at 40° gives HCl . *p*- $C_6H_4 \cdot Br \cdot OPh$ and *o*- $OMe \cdot C_6H_4 \cdot OPh$ give no phenoxthionine. Chlorination of phenoxthionine gives a (? 1-)*Cl*-derivative, m.p. 81—82° (*dioxide*, m.p. 178—179°). *Ph o*-, b.p. 152—153°/15 mm., m.p. 39—40°, m-, b.p. 168—169°/30 mm., and *p*-chlorophenyl ether, b.p. 161—162°/19 mm., are prepared. R. S. C.

Pyrrole derivatives. III. I. J. RINKES (Rec. trav. chim., 1937, **56**, 1224—1228).—Interaction of $\text{NH}_2\cdot\text{CH}_2\cdot\text{CHO}$ and $\text{Et}_2\text{C}_2\text{O}_4$ in aq. KOH yields 3-carbethoxypyrrole-2-carboxylic acid, m.p. 146—147°, converted by $\text{Cu}(\text{CrO}_2)_2$ in boiling quinoline into 3-carbethoxypyrrole, m.p. 48—49°, hydrolysed (KOH) to pyrrole-3-carboxylic acid, m.p. 147—148° (*Me* ester, m.p. 87°). J. D. R.

N-Phenylpyrroles from phenacyl-lævulic acid. M. G. HOLDSWORTH and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1937, **70**, 431—436).—Phenacyl-lævulic acid (I), when boiled with NaOH and the product acidified, yields 3-phenyl- Δ^2 -cyclopenten-1-one-2-acetic acid, m.p. 138° (phenylhydrazone, m.p. 180—181°; semicarbazone, m.p. 224—225°), reduced (Na-Hg) to the cyclopentane acid, m.p. 132° (phenylhydrazone, m.p. 165°; semicarbazone, m.p. 198—199°). Condensation of (I) with arylamines at 100° (in EtOH if necessary) yields 1-aryl-2-phenylpyrrole-5- β -propionic acids: 1-phenyl-, m.p. 175° (*Et* ester, m.p. 102—103°; hydrazide, m.p. 142°); 1-o-chloro-, m.p. 170°; -bromo-, m.p. 191°; -methoxy-, m.p. 162°; -ethoxy-, m.p. 149°; -xenyl-, m.p. 73°, and -carboxy-phenyl-, m.p. 191°; 1- α -naphthyl-, m.p. 130°, 1-8'-quinolyl-, m.p. 182°. A. Li.

Purification of piperidine. E. S. COOK (J. Amer. Chem. Soc., 1937, **59**, 2661).—Piperidine, prepared by catalytic hydrogenation, is purer than that prepared by electrolytic reduction, but also gives "diothane" of low activity (cf. A., 1937, II, 466, 467). R. S. C.

Diaminomethane and its derivatives. II. 2-Aminopiperidine and the reduction products of 2-aminopyridine. A. V. KIRSANOV and J. N. IVASCHTSCHENKO (J. Gen. Chem. Russ., 1937, **7**, 2092—2098).—2-Aminopyridine (I) in EtOH and Na yield piperidine, cadaverine, and NH_3 ; 2-aminopiperidine is not obtained, and is shown on theoretical grounds to be so unstable as not to be able to exist under the conditions of the experiment. Hydrogenation of (I) (PtO_2) in Ac_2O yields 2-acetamido-1-acetpiperidide, m.p. 122—123°. 2-Diphenylaminopiperidine, m.p. 131—133°, is prepared analogously. R. T.

Conductivities of metallic complexes.—See A., I, 83.

2-Ketoquinuclidine and a new synthesis of quinuclidine. G. R. CLEMO and T. P. METCALFE (J.C.S., 1937, 1989—1990).—*Et* piperidine-1-acetate-4-carboxylate, b.p. 134—136°/1 mm., obtained from *Et* piperidine-4-carboxylate and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, undergoes the Dieckmann reaction to form 2-ketoquinuclidine, m.p. 138° [methiodide, m.p. 310° (decomp.); picrate, m.p. 210°], which is reduced (Wolff or Clemmensen) to quinuclidine. F. R. S.

Hydrogenation of some N-substituted 2-pyridones with Raney nickel. J. A. GAUTIER (Compt. rend., 1937, **205**, 614—616; cf. A., 1937, II, 75).—Many 2-pyridones in EtOH with H_2 -Raney Ni at room temp. and pressure absorb 4 H at a const. rate to give the corresponding piperidones in theoretical yield. The following are prepared: N- β -hydroxyethyl-, m.p. 39—40° (aurichloride, m.p. 169°; picrate,

m.p. 71°; phenylcarbamate, m.p. 118°), - γ -propoxypropyl- (I), b.p. 193°/13 mm., and - γ -isoamyloxypropyl-2-piperidone (II), b.p. 208°/14 mm. (I) and (II) are feebly basic and are decomposed by acid chlorides. J. L. D.

4-Hydroxypyridinebetaine. A. KIRPAL and F. POISEL (Ber., 1937, **70**, [B], 2367—2369).—4-Hydroxypyridine and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ in boiling, slightly alkaline solution give 4-hydroxypyridinebetaine, $\text{OH}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{CH}\cdot\text{CH} \end{smallmatrix}\text{N}\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}\text{CO}$, decomp. 270° [hydrochloride; Na (+2.5 H_2O), m.p. 122°, and Ag (+1 H_2O), decomp. 252°, salts]. Its constitution follows from its conversion into 4-methoxypyridinebetaine, m.p. 182° (decomp.), and thence by conc. aq. NH_3 at room temp. into 4-aminopyridinebetaine, decomp. 315°, also derived from 4-aminopyridine and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$. H. W.

Manufacture of 4 : 6-diamino-2-alkylpyridines.—See B., 1938, 39.

Derivatives of 3-diazo-2-phenylindole. I. F. ANGELICO and S. CAPUANO. II. S. CAPUANO (Gazzetta, 1937, **67**, 633—637, 710—714).—I. 3-Amino-2-phenylindole (I) (new prep. from oximinophenylindole, NH_3 , and H_2S) with NaNO_2 gives, in addition to 3-diazo-2-phenylindole (II) (A., 1905, i, 940), 3-azo-2-phenylindole (?), $\text{C}_{26}\text{H}_{20}\text{N}_4$ (III), red, m.p. 263° (decomp.). The product from (II) and 25% H_2SO_4 , previously regarded (*loc. cit.*) as (III), is probably hydrazophenylindole (IV), m.p. 271° (decomp.), reddish-yellow.

II. The constitutions suggested above for (III) and (IV) are confirmed. With $\text{NH}_2\text{OH}\cdot\text{HCl}$, $\text{N}_2\text{H}_4\cdot\text{HCl}$, or $\text{NHPh}\cdot\text{NH}_2$ in EtOH, (II) evolves N_2 and yields (IV) and (I), which are also obtained by reduction of (III) (aq. NH_3 - H_2S). Oxidation of (IV) by N_2O_4 or of (I) by amyl nitrite gives (III). With boiling HCl, (II) yields (IV) and another substance. E. W. W.

Formation of the compound between tungstic acid and 8-hydroxyquinoline.—See A., I, 93.

Quinoline derivatives. III. (SIGNA.) L. MONTI (Gazzetta, 1937, **67**, 624—628; cf. A., 1932, 1261).—2-Hydroxy-4 : 8-dimethylquinoline and $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ in conc. H_2SO_4 yield the N-chloroacetyl derivative, m.p. 260—262° (decomp.), of 2-hydroxy-4 : 8-dimethyl-3-quinolylmethylamine [hydrochloride; picrate, m.p. 263—264° (decomp.)]. 4-Hydroxy-2 : 8-dimethylquinoline similarly gives the N-chloroacetyl derivative, m.p. 252—254° (decomp.), of 4-hydroxy-2 : 8-dimethyl-3-quinolylmethylamine, no. m.p. <280° (picrate, decomp. 180—190°). E. W. W.

Quinoline compounds as bases of medicinal compounds. VI. Antimalarial compounds with the side-chain in position 4. O. J. MAGIDSON and M. V. RUBTZOVA (J. Gen. Chem. Russ., 1937, **7**, 1896—1908).—6-Methoxyquinoline and BzO_2H in CHCl_3 (18 hr. at 0—2°) yield 6-methoxyquinoline N-oxide, m.p. 108—109° (+2 H_2O , m.p. 88—89°; hydrochloride, m.p. 193—194°; picrate, m.p. 173.5—174.5°), which with SO_2Cl_2 at 60° gives a mixture of di- and trichloro-6-methoxyquinoline, whilst with POCl_3 the product consists of 2- (I) and 4-chloro-6-methoxy-

quinoline (II). $\text{NH}_2\cdot\text{CHMe}\cdot[\text{CH}_2]_3\cdot\text{N}(\text{Et})_2$ and (II) when heated at 165–170° (6.5 hr.) yield 4-(8-diethylamino- α -methylbutyl)amino-6-methoxyquinoline (III), m.p. 127–127.5° (picrate, m.p. 182–183.5°), whilst under similar conditions (I) gives a mixture of 2-(8-diethylamino- α -methylbutyl)amino-6-methoxyquinoline, b.p. 180°/2 mm. (hydrochloride, m.p. 98–101°; picrate, m.p. 153.5–155°), and α -diethylamino-8-di-(6-methoxy-2-quinolyl)aminopentane, m.p. 77.5–78.5° (picrate, m.p. 187.5–188.5°). The following compounds were prepared analogously to (III): 4- (IV), m.p. 90–90.5° (picrate, m.p. 198–199°), and 2-(8-diethylamino-butyl)amino-, b.p. 187–192° (picrate, m.p. 182.5–183.5°; dihydrochloride, m.p. 187–188°); 4- (V), an oil (picrate, m.p. 210–212°, and its acetate, m.p. 205–207°), and 2-(γ -diethylamino- β -hydroxypropyl)-amino-6-methoxyquinoline, m.p. 65–66° (hydrochloride, m.p. 99–102°; picrate, m.p. 190.5–192°). The 2- NH_2 -quinoline derivatives had no antimalarial action; the activity of the 4- NH_2 -compounds rises in the order (IV) < (III) < (V). R. T.

Thalleioquinine reaction. III. (SIGNA.) L. MONTI (Gazzetta, 1937, 67, 621–624; cf. A., 1936, 613).—8-Hydroxy-7-methylquinoline (I) and $\text{OH}\cdot\text{CH}_2\cdot\text{NHBz}$ in conc. H_2SO_4 yield benz-8-hydroxy-7-methyl-5-quinolylmethylamide, m.p. 175–176°. With CH_2O in 15% NaOH , (I) gives 8-hydroxy-7-methylquinolylmethyl alcohol, decomp. 150–160°. Since these products fail to give the thalleioquinine reaction, unlike the product (II) from 6-hydroxyquinoline, it is concluded that (II) is not substituted in position 7, but is benz-6-hydroxy-5-quinolylmethylamide (cf. A., 1932, 1261–1262). E. W. W.

Catalytic condensation of acetylene with aromatic amines. N. KOZLOV (J. Gen. Chem. Russ., 1937, 7, 1860–1865).— NH_2Ph in COMe_2 and C_2H_2 in presence of HgCl_2 (7 hr. at room temp.) yield 2-methyl- and 2:4-dimethyl-quinoline. The products obtained similarly from *o*-, *m*-, and *p*-toluidine are respectively 2:8-di- and 2:4:8-tri-, 2:4:5-tri-, and 2:6-di- and 2:4:6-tri-methylquinoline, m.p. 38° (hydrochloride, m.p. >240°; picrate, m.p. 203°). $\text{NPh}\cdot\text{CHMe}$ is an intermediate product in the above condensations. R. T.

6:9-Diamino-2-ethoxyacridine methanesulphonate.—See B., 1938, 105.

Formation of tetrahydrophenanthroline as a by-product in the Skraup synthesis of *p*-phenanthroline. J. P. WIBAUT, C. W. F. SPIERS, and J. L. OUWELTJES (Rec. trav. chim., 1937, 56, 1218–1223).— $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$, glycerol, and H_3AsO_4 yield *p*-phenanthroline and the H_4 -compound, m.p. 151.2–151.6°, described by Matsumura (A., 1935, 631) (Bz_1 derivative, m.p. 180.7–181°; Ac_1 derivative, m.p. 121°), which is probably 1:2:3:4-tetrahydrophenanthroline. J. D. R.

Yellow and colourless modifications of benzylidene- and *N*-3-methylbenzylidene-hydantoin. (MISSSES) D. A. HAHN and M. M. ENDICOTT (J. Amer. Chem. Soc., 1937, 59, 2741–2742).—The substances named exist each in yellow and colourless forms, otherwise similar, which are interconvertible. The yellow form is stable in acid, the colourless in alkaline,

solution; they may thus be lactam and lactim forms, respectively. R. S. C.

Additive products of antipyrine and pyrimidone. G. LA PAROLA (Gazzetta, 1937, 67, 645–647).—Antipyrine (I) with maleic anhydride (II) in moist air gives the (1:1) maleate, m.p. 115°. Pyrimidone (III) when heated with (II) forms the (1:1) maleate, m.p. 123–124°. With picric acid these yield the picrates of (I) and (III). E. W. W.

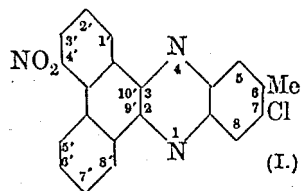
Rearrangement of some β -allyloxycrotonic esters. W. M. LAUER and (MISS) E. I. KILBURN (J. Amer. Chem. Soc., 1937, 59, 2586–2588).—Rearrangement of *Et* β -cinnamyloxycrotonate (I) by NH_4Cl at 110° gives *Et* α -(α' -phenylallyl)acetoacetate (II), different from the *Et* α -cinnamylacetoacetate (III), b.p. 156–158°/0.5–1 mm., obtained from $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$, NaOEt , and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$. Thus *O*-alkylation does not occur by way of the *O*-ether. *Et* β -allyloxycrotonate [from a mixture (IV) of *Et* β -chloro-crotonate and -isocrotonate, NaNH_2 , and $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$], m.p. 7–11°, gives *Et* α -allyl-acetoacetate (identified by conversion into the pyrazolone), but the mechanism of this change is obscure. Prep. of (I) from (IV) gives a low yield. CHPhEtBr and $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ give *Et* α -(α' -phenyl-*n*-propyl)-acetoacetate, b.p. 127–129°, converted by N_2H_4 into 4- α -phenylpropyl-3-methyl-5-pyrazolone (V), m.p. 193–194°. With N_2H_4 or $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ (III) gives 4-cinnamyl-3-methyl-5-pyrazolone, m.p. 214–219°, hydrogenated (H_2 - PtO_2) to 4- γ -phenylpropyl-3-methyl-5-pyrazolone, m.p. 176–177.5°, also obtained from *Et* α - γ' -phenylpropylacetoacetate. 4- α -Phenylallyl-3-methyl-5-pyrazolone, m.p. 180–182°, is obtained from (II) and N_2H_4 or from (I), N_2H_4 , and a little HCl , and, when reduced, gives (V). R. S. C.

Derivatives of piperazine. XIII. Analogues of ephedrine containing the *N*-phenylpiperazine nucleus. B. L. HAMPTON and C. B. POLLARD (J. Amer. Chem. Soc., 1937, 59, 2570–2572; cf. A., 1938, II, 30).—*N*-Phenyl-*N'*-phenacylpiperazine gives *N*-phenylpiperazine and COPhMe with Al-Hg in H_2O or N_2H_4 at 185–195°, but with H_2 - Pd-C in dil. HCl gives an 85% and with NaOEt-EtOH at 185–195° gives an 80% yield of *N*-phenyl-*N'*- β -hydroxy- β -phenylethylpiperazine (I), m.p. 110–111° [dihydrochloride, m.p. 210–212°; *Bz* derivative, an oil (dihydrochloride, m.p. 228–230°)]. With N_2H_4 , NaOEt , and EtOH mixtures of (I) and *N*-phenyl-*N'*- β -phenylethylpiperazine, m.p. 77–78° (dihydrochloride, m.p. 220–222°), are obtained. *N*-Phenyl-*N'*- β -hydroxy- β -*p*-tolylethylpiperazine, m.p. 127–128° [dihydrochloride, m.p. 199–201°; *Bz* derivative, an oil (dihydrochloride, m.p. 219–221°)], is similarly obtained. R. S. C.

Cyanine dye series. IX. 4:4'-Pyridocyanines and 4-pyrido-4'-cyanines. R. H. SPRAGUE and L. G. S. BROOKER (J. Amer. Chem. Soc., 1937, 59, 2697–2699; cf. A., 1937, II, 124).—4-Iodopyridine meth- and eth-iodide could not be obtained. PhSH and 4-chloropyridine give 4-phenylthiolpyridine, b.p. 128–129°/3 mm., the methiodide, m.p. 174–176°, (decomp.), of which with γ -picoline metho-*p*-toluenesulphonate and NEt_3 in Pr^nOH leads to 1:1'-dimethyl-

4:4'-pyridocyanine [bis-1-methyl-4-pyridinemethine-cyanine] perchlorate (I), m.p. 263—265° (decomp.) [corresponding picrate, m.p. 231—232° (decomp.)], also obtained similarly from 4-chloropyridine methiodide, m.p. 161—163° (decomp.). 4-Phenylthiol-pyridine ethiodide, m.p. 178—180° (decomp.), gives similarly 1:1'-diethyl-4:4'-pyridocyanine [bis-1-ethyl-4-pyridinemethinecyanine] perchlorate (II), m.p. 196—198° (decomp.), not obtained from 4-chloropyridine ethiodide. By either method lepidine methiodide gives 1:1'-dimethyl-4-pyridino-4'-cyanine [1-methyl-4-pyridine-1'-methyl-4'-quinolinemethinecyanine] perchlorate (III), m.p. 220—221° (decomp.), and by the thiol method the analogous diethyl-perchlorate (IV), m.p. 172—174° (decomp.). The dyes are strong photographic sensitizers with absorption max. in MeOH as follows: (I) 5025 Å., (II) 5050 Å., (III) 5285 Å. (secondary max. 5050 Å.), and (IV) 5300 Å. (secondary max. 5450 Å.), and only (IV) causes fogging. R. S. C.

Dyes derived from phenanthraquinone. D. PRASAD, S. C. SEN, and P. C. DUTTA (Ber., 1937, 70, [B], 2363—2365).—Deeply coloured dyes derived from phenanthraquinone are described. 4-Nitrophenanthraquinone and 6-chloro-3:4-diaminotoluene in hot AcOH yield



7-chloro-4'-nitro-6-methyl-9':10'-2:3-phenanthrenoquininoxaline (I), m.p. 227°. The corresponding -2'-nitro-, m.p. >300°, -4':5'-dinitro-, m.p. 268°, -2':7'-dinitro-, m.p. >300°, -2'-bromo-, m.p. 242°, -??-dibromo-, m.p. >300°, -2'-hydroxy-, m.p. 245°, -2'-amino-, m.p. 291°, and -4'-amino-, m.p. 134°, -derivatives are prepared analogously. Treatment of (I) with Cu powder and boiling NH₂Ph affords 4'-nitro-7-anilino-6-methyl-9':10'-2:3-phenanthrenoquininoxaline, m.p. 178°. Analogous methods lead to the production of the corresponding 2'-nitro-, m.p. 242°, 4':5'-dinitro-, m.p. 136°, 2':7'-dinitro-, m.p. 205°, 2-amino-, m.p. 253°, and -2-hydroxy-, m.p. 202°, -compounds. 2':7'-Dianilino-6-methyl-9':10'-2:3-phenanthrenoquininoxaline has m.p. 157°. H. W.

Symmetry of certain types of benzotriazoles. W. M. LAUER, W. F. FILBERT, and G. E. ULLYOTT (J. Amer. Chem. Soc., 1937, 59, 2584—2586).—2-p-Hydroxyphenyl-6- (I), m.p. 242—243°, and -5-methylbenzotriazole 1-oxide (II), m.p. 265—266° (decomp.), differ, but with SnCl₂ give the same 2-p-hydroxyphenyl-5- (or -6-)methylbenzotriazole, demonstrating the equivalence of positions 5 and 6 of benzotriazoles. 3:1:4-NO₂-C₆H₃Me-NH₂ (III) is converted into 2-nitro-4'-hydroxy-4-methylazobenzene, m.p. 156—157°, which with Na₂S₂O₄ yields (I). With H₂S₂O₈ (III) gives 3:1:4-NO₂-C₆H₃Me-NO, oxidised by HNO₃ to 1:3:4-C₆H₃Me(NO₂)₂, which with NH₃-EtOH gives 4:1:3-NO₂-C₆H₃Me-NH₂; under clearly defined conditions this affords 2-nitro-4'-hydroxy-5-methylazobenzene, m.p. 129—130°, and thence (II) using Na₂S₂O₄. M.p. are corr. R. S. C.

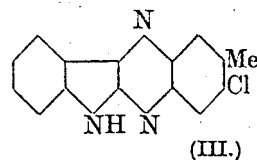
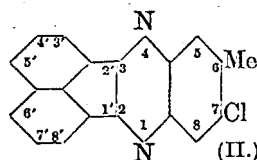
Triazines. I. Reactions of isocyanuric esters with organo-magnesium compounds. H. So-

BOTKA and (Miss) E. BLOCH (J. Amer. Chem. Soc., 1937, 59, 2606—2608).—Me₃ cyanurate (prep. by CH₂N₂), m.p. 174°, with MgRBr in Et₂O gives 2-hydroxy-4:6-diketo-2-phenyl-1:3:5-trimethyl- (I), m.p. 158—159° (decomp.), -1:3:5-trimethyl-2-ethyl-, m.p. 112—113°, and -1:3:5-trimethyl-2-n-propyl-1:3:5-triazine (II), m.p. 129°. These products form tribromides, m.p. 196°, 128°, and 151°, respectively, formulated as [NMe<CO-NMe>NR]⁺Br₃⁻, and (II) gives an analogous tri-iodide, m.p. 112—115°. In C₆H₆ some (I) with CPh₃·OH is obtained. No reaction occurs between (I) and MgPhBr. R. S. C.

γ-Triazines. XXXVI. Aminothiolisohutyl-triazine and the corresponding aminohydroxy-derivative. V. GALEA and A. OSTROGOVICH (Gazetta, 1937, 67, 664—668; cf. A., 1930, 368; 1935, 1255).—K thiolisovalerate, from Bu^tCOCl and KSH, and cyanoguanidine yield 4-amino-6-thiol-2-isobutyl-1:3:5-triazine, m.p. 269—270° (decomp.) [hydrochloride (+H₂O); picrate, m.p. 174—175° (decomp.)], the Ag salt, m.p. 150° (decomp.), of which forms a complex salt (explodes when heated) with AgNO₃; it is converted by KOH-H₂O₂ into 4-amino-6-hydroxy-2-isobutyl-1:3:5-triazine, m.p. 263—264° (decomp.) [Ag salt; hydrochloride; sulphate; picrate, m.p. 217—218° (decomp.)]. E. W. W.

Syntheses in the pyrazolinoquinoline series. A. KOCWA (Bull. Acad. Polonaise, 1937, A, 232—238).—α-C₁₀H₇·NH₂·HCl, 1-phenyl-3-methylpyrazolone, and POCl₃ at 260—270° give 5-α-naphthylimino-1-phenyl-3-methyl-4:5-dihydropyrazole (I), m.p. 146—147° (hydrochloride, m.p. 206°; picrate, m.p. 184°), the methiodide, m.p. 220°, of which with NaOH gives 5-α-naphthyliminoantipyrene, m.p. 161—162°. With PhNCO at 270° or PhNCS at 230—235° (I) gives 4-anilino-7:8-benzo-1'-phenyl-3'-methylpyrazolino-5':4'-2:3-quinoline, m.p. 198° [hydrochloride, m.p. 205°; NO-derivative, m.p. 184—185° (decomp.)], which is hydrolysed by 50% KOH-EtOH at 200—220° to 4-hydroxy-7:8-benzo-1'-phenyl-3'-methylpyrazolino-5':4'-2:3-quinoline, m.p. 281—282°, also obtained by hydrolysis of 4-α-naphthylamino-7:8-benzo-1'-phenyl-3'-methylpyrazolino-5':4'-2:3-quinoline, m.p. 225° [obtained from (I) and C₁₀H₇·CNO at 230°]. R. S. C.

Dyes derived from acenaphthenequinone and isatin. D. PRASAD and P. C. DUTTA (Ber., 1937, 70, [B], 2365—2366).—Acenaphthenequinone and 6-chloro-3:4-diaminotoluene (I) afford 7-chloro-6-methyl 1':2'-2:3-acenaphthylenequininoxaline (II), m.p.



287°. 7-Chloro-5'-nitro-, m.p. 258°, and -5':6'-dinitro-, m.p. 290°, -6-methyl-1':2'-2:3-acenaphthylenequininoxaline are described. 7-Chloro-6-methyl-2':3'-2:3-indoloquininoxaline, m.p. >300° (III), is derived from (I) and isatin and is converted by Cu powder and boiling NH₂Ph into 7-anilino-6-methyl-2':3'-

2:3-indoloquinoxaline, m.p. 260°. 7-Anilino-6-methyl-1':2'-2:3-acenaphthylenoquinoxaline has m.p. 243°. II. W.

Constitution of the purine nucleosides. V. Adenine thiomethylpentoside. R. FALCONER and J. M. GULLAND (J.C.S., 1937, 1912—1913).—The ultra-violet absorption spectra of adenine thiomethylpentoside in aq., acid, and alkaline solutions closely resemble those of adenosine and 9-methyladenine in similar conditions and are unlike those of 7-methyladenine; hence, the thio-sugar is attached to position 9. F. R. S.

Ammoniacal absorption spectrum of stercobilin and urobilin and its relationship to the constitution of bilirubinoid pigments. L. HEILMEYER, H. GEIGER, and R. SCHULTZE (Biochem. Z., 1937, 294, 90—94).—The absorption spectrum of stercobilin hydrochloride (obtained from hæmolytic jaundice stool) in 1% aq. NH_3 is compared with that of bilirubin (I) in CHCl_3 ; both solutions show a broad band about 450 μ . Comparison of the absorption spectra of (I), mesobilirubin, and xanthobilirubic acid in EtOH and stercobilin in aq. NH_3 , and their mol. extinction coeffs. suggests that in the stercobilin mol. there is a double linking attached to one pyrrolidine nucleus. C. C. N. V.

Preparation of 1-methylbenzoxazole. M. A. PHILLIPS (J.S.C.I., 1937, 56, 474r).—1-Methylbenzoxazole is obtained in 74% yield from $o\text{-NH}_2\text{-C}_6\text{H}_4\text{-OH}$ and Ac_2O ; the method used presents advantages over that of Beilenson (A., 1937, II, 392). (Cf. Newbery and Phillips, A., 1928, 311.)

isoOxazole and pyrazole groups. I. C. MUSANTE (Gazzetta, 1937, 67, 682—690).— $\text{CMe:C-CO}_2\text{Et}$ and CHPh:N-OH (I) at 120—130° yield 4-benzylidene-3-methyl-5-isooxazolone, m.p. 145°, also obtained from (I) and $\text{CH}_3\text{Ac-CO}_2\text{Et}$ (ZnCl_2). Similarly 4-anisylidene-3-methyl-5-isooxazolone, m.p. 175°, is obtained by either method. $\text{CPh:C-CO}_2\text{Et}$ (II) and CHPh:N-NHPh at 170—180° give Et 1:3:5-triphenylpyrazole-4-carboxylate (A., 1929, 196); the 1:5-diphenyl-3-p-nitrophenyl compound, new m.p. 177° (cf. loc. cit.), is obtained similarly. $\text{CH}_2\text{Bz-CO}_2\text{Et}$ and CHEt:N-NHPh (III) yield (ZnCl_2) the Et ester, m.p. 119°, of 1:5-diphenyl-3-ethylpyrazole-4-carboxylic acid, m.p. 192°. From (II) and (III) at 140°, a substance, $\text{C}_{33}\text{H}_{28}\text{O}_2\text{N}_4$ (2:2'-propylidene-1:5:1':5'-tetraphenylbis-3:3'-pyrazolone?), m.p. 192—194°, is obtained, hydrolysed to EtCHO and 1:5-diphenyl-3-pyrazolone. E. W. W.

Oximinopyrroles. VIII. Action of acids. T. AJELLO (Gazzetta, 1937, 67, 728—738; cf. A., 1937, II, 524).—Oximinotriphenylpyrrole and H_2SO_4 in EtOH at the b.p. give 3-benzoyl-4:5-diphenylisooxazole, m.p. 158° (or 168°?) [p-nitrophenylhydrazone, m.p. 140—141°; semicarbazone, m.p. 227°; oxime, m.p. 162° (Bz derivative, m.p. 122°)], and a yellow substance, m.p. 242°. Oximinodiphenylpyrrole yields 3-benzoyl-5-phenylisooxazole, m.p. 89—90° [semicarbazone, m.p. 182°; oxime, m.p. 115° (Bz derivative, m.p. 140°); p-nitrophenylhydrazone, m.p. 180°; hydrazone, m.p. 200°], and a yellow substance, m.p.

235°. Oximinophenylmethylpyrrole yields 3-acetyl-5-phenylisooxazole, m.p. 105° (p-nitrophenylhydrazone, m.p. 175—178°). Brown or black amorphous products are also formed in the above reactions.

E. W. W.

Derivatives of morpholine. I. Addition to conjugated systems. I. V. E. STEWART and C. B. POLLARD (J. Amer. Chem. Soc., 1937, 59, 2702).—Morpholine and the appropriate ketone, CHAr:CH-COAr , in hot heptane give Ph β -N-morpholino- β -phenyl-, m.p. 80.5—81°, - β -p-tolyl-, m.p. 90—90.5°, and - β -p-chlorophenyl-ethyl ketone, m.p. 89.5—90°, p-tolyl, m.p. 90—90.5°, and p-bromophenyl β -N-morpholino- β -phenylethyl ketone, m.p. 99.6—100.2°. Some chalkones did not give such compounds owing to the ease of dissociation. The di-p-tolyl ketone forms the compound, but this dissociates when recrystallised. M.p. are corr. R. S. C.

Morpholine as a reagent for mobile halogen atoms and nitro-groups. R. H. HARRADENCE and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1937, 70, 406—412).—Compounds containing reactive halogen atoms or NO_2 -groups when boiled with excess of morpholine for 2—3 hr. give well-cryst. derivatives of N-phenylmorpholine: 2-nitro-, m.p. 42°, 4-nitro-, m.p. 149—150°, and 2:4-dinitro-, from the corresponding Cl-compounds; 4-chloro-2-nitro-, m.p. 47°, and 2-chloro-4-nitro-, m.p. 127°, from 2:5- and 3:4- $\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$, respectively; 4:6-dibromo-2-nitro-, m.p. 105° (the corresponding piperidine derivative, m.p. 73°), from 3:5-dibromo-2-iodonitrobenzene, m.p. 82° (prepared from $\text{NO}_2\text{-C}_6\text{H}_3\text{Br}_2\text{-NH}_2$); 2-nitro-6-methyl-, m.p. 135—136°, from 1:2:6- $\text{C}_6\text{H}_3\text{MeI-NO}_2$ (5 hr. in boiling EtOH); 2:4-dinitro-6-carboxy-, m.p. 203—204° (decomp.) (Me ester, m.p. 106°), from chlorodinitrobenzoic acid; 2-nitro-4:5-dimethoxy-, m.p. 115—116°, from 4-bromo-5-nitro- or 4:5-dinitroveratrole; and 2-nitro-4:5-di-n-butoxy-, m.p. 75—76°, from 1:2:4:5- $\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{OBU}^n)_2$. Morpholine is less reactive than piperidine towards o-chloro- and o-bromo-nitrobenzene. A. LI.

Nicotinylmorpholine. R. H. HARRADENCE and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1937, 70, 428—430).—Prolonged boiling of Et nicotinate with excess of morpholine gives nicotinylmorpholine, b.p. 192°/6 mm. (picrate, m.p. 174—175°; methiodide, m.p. 211—212°; aurichloride, m.p. 168°). A. LI.

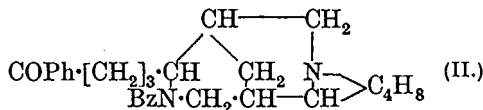
Alkaloids of Arundo donax. L. J. MADIN-AVETIA (J.C.S., 1937, 1927—1929; cf. A., 1937, II, 125).—The alkaloid $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N(NMe)}$ is called donaxarine, m.p. 217°. Gramine (donaxine) with MeI-MeOH-KOH gives NMe_4I and 3-methoxymethylindole, m.p. 99—100°, and with MeI-MeOH forms NMe_3 and a substance similar to 3-hydroxymethylindole, m.p. 90°, obtained by reduction ($\text{PtO}_2\text{-H}_2$) of indole-3-aldehyde. Gramine and EtI-EtOH-KOH yield 3-ethoxymethylindole, m.p. 93—94°, and with EtI-COMe₂, gramine ethiodide, m.p. 176°, is obtained. There are indications of the presence of a third alkaloid with phenolic properties. F. R. S.

Cactus alkaloids. New alkaloid from mezcal buttons. E. SPÄTH and J. BRUCK (Ber., 1937, 70, [B], 2446—2450).—The non-phenolic bases of

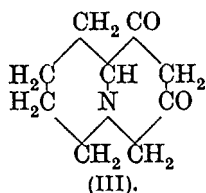
fresh mezeal buttons are worked up roughly as sulphates and hydrochlorides and the mother-liquor from these salts is separated into seven base fractions by partial extraction with HCl in presence of NaCl. From the appropriate fraction mezcaine is mainly separated as the sulphate; the bases obtained from the mother-liquors are converted into their hydrochlorides, which by repeated treatment with MeOH-Et₂O yield *N-methylmezcaline hydrochloride*, m.p. 201–202° (corresponding *picrate*, m.p. 177.5–178.5°, *trinitro-m-tolylloxide*, m.p. 189.5–190.5°, and *p-nitrobenzoyl* derivative. *N-Methylmezcaline* [methyl-β-3:4:5-trimethoxyphenylethylamine] is obtained synthetically by converting mezcaline by PhCHO at 100° into *benzylidenemezcaline*, b.p. 190° (bath)/0.03 mm., and thence into the *methiodide*, which is readily hydrolysed to the required base. All the known alkaloids of this series are derivatives of β-3:4:5-trihydroxyphenylethylamine. H. W.

Tobacco alkaloids. XIII. New bases of tobacco. E. SPÄTH and F. KESZTLER (Ber., 1937, 70, [B], 2450–2454).—Crude nicotine, freed from *l*- and *dl*-nornicotine, is transformed into its *H d*-tartrate, whereby the bulk of the nicotine is removed. The base, isolated from the mother-liquor of this salt, is allowed to crystallise again as *H d*-tartrate from a correspondingly smaller vol. of solution. Frequent repetition of this process leaves a small amount of a basic mixture, separated further by treatment with HCl in presence of NaCl and transformation of the fractions into the picrates. The presence of nicotine is thus established. *l-N-Methylanatabine*, [α]_D²⁵ –171.4° in MeOH (*picrate*, m.p. 207–208°; *trinitro-m-tolylloxide*, m.p. 228–229° after softening at 226°), and *l-N-methylanabasine*, [α]_D²⁵ –137.3° in MeOH, are also present; their prep. by the action of CH₂O and HCO₂H on anatabine and anabasine, respectively, is described. H. W.

Lupin alkaloids. XV. Oxidative degradation of phenyldehydrosparteine. Constitution of sparteine and lupanine. K. WINTERFELD and M. SCHIRM (Arch. Pharm., 1937, 275, 630–662; cf. A., 1937, II, 526).—Degradation products are obtained which confirm the structure previously assigned to sparteine. Phenyldehydrosparteine (I) and BzCl in KOH-H₂O-COMe₂ give *N-benzoyl-ω-phenylsparteone*



(II), an oil (*picrate*, m.p. 87–88°; *methiodide*, m.p. 73–75°, stable to KMnO₄), which gives deep-seated oxidation products with KMnO₄,

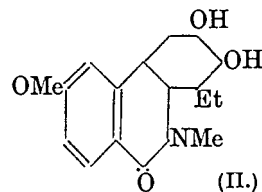
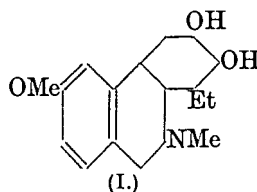


but with CrO₃-H₂SO₄ under various conditions gives (CH₂·CO₂H)₂, NH₂·[CH₂]₄·CO₂H, 3:5-diketo-octahydropyridocoline (III), an oil [*aurichloride*, m.p. 174° (decomp.); *reineckate*, decomp. 206–208°;

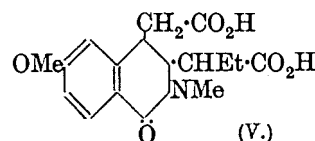
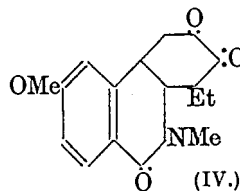
Me ether of the enolic form, an oil (*reineckate*, decomp. 178–180°), absorbs 1 H₂ when hydrogenated; gives oily ketone derivatives; gives an oily pyrazoline], and the lactone

(IV), CH₂ < $\begin{array}{c} \text{CH} \cdot \text{C} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{N} \\ \text{CO} \cdot \text{O} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH}_2 \end{array} \rangle \text{C}_4\text{H}_8$, an oil [*reineckate*, sinters at 153°; unsaturated towards KMnO₄; gives an impure *Me* ester (*reineckate*, decomp. 85°)]. MnO₂-H₂SO₄ gives (III) and (IV), and HNO₃ gives (III). With HNO₃ (I) gives BzOH and (III). Clemmensen reduction of (III) gives a base, C₁₃H₂₃N₂ (*picrate*, m.p. 226°; *aurichloride*, decomp. 182–183°), *N*-methyl-2-piperidone, and a little sparteine (derived from lupanine present as an impurity). With HI-red P (III) gives (?) norlupinan, and electrolytic reduction gives piperidine. R. S. C.

Lycoris alkaloids. XI. Constitution of lycoramine. H. KONDO and S. ISHIWATA (Ber., 1937, 70, [B], 2427–2437).—Lycoramine (I), m.p. 120°, [α]_D²⁵ –98.2° [*platinichloride*, decomp. 245°; *perchlorate*, m.p. 138–139°; *methiodide*, decomp. 308°, or (+MeOH), m.p. 220° (decomp.)], contains 1 NMe, 1 OMe, and 2 OH (*lycoramine diacetate*, m.p. 95°). It does not contain a phenolic OH since it is insol. in alkali and does not give a OMe-derivative with Me₂SO₄. Lycoramine methohydroxide is very stable towards boiling 30% KOH but gives a little *methine* base, C₁₇H₂₅O₃N·CH₂ (*picrate*, m.p. 148°; *methiodide*, decomp. 213–214°). Lycoramine methochloride is transformed by the prolonged action of Na-Hg and

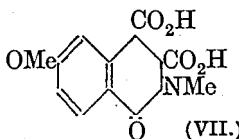
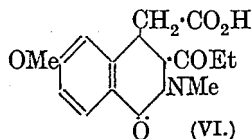


boiling H₂O into *lycoraminemethylhydromethine-A*, C₁₈H₂₉O₃N, m.p. 96°, [α]_D²⁵ –54.2° in EtOH (*hydrochloride*, m.p. 210–211°; *phenylurethane*, m.p. 150–151°; *methiodide*, decomp., 152–153°), and *lycoraminemethylhydromethine-B*, m.p. 145°, [α]_D²⁵ +43.6° in EtOH (*hydrochloride*, m.p. about 210°; *methiodide*, decomp. 105–110°). Oxidation of lycoraminemethylhydromethine methohydroxide with cold, alkaline KMnO₄ gives EtCO₂H. Oxidation of (I) with cold KMnO₄ yields H₂C₂O₄, *m*-methoxyphthalic anhydride, and a neutral substance (II), m.p. 253°, [α]_D²⁵ +73.7° in CHCl₃, which contains 1 NMe, 1 OMe, and 2 OH (*Ac*₂ derivative). HIO₄ or Pb(OAc)₄ has little action on (II), which affords 1-methylphenanthridine (III), m.p. 80–82° after softening at about 78° [*picrate*, m.p. 217–218°; *styphnate*, m.p. 148° (decomp.)]; double compound with HgCl₂, m.p. 190–195°, when distilled with Zn dust. [The synthesis of (III) from *o*-C₆H₄Br·CHO, 1:3:2-C₆H₃BrMe·NH₂, and Cu powder at 210° is recorded.] Oxidation of (II) with CrO₃ in



AcOH yields an *α*-diketo-compound (IV), m.p. 220°, [α]_D²⁵ +275.5° [*oximino*-derivative, m.p. 189–190°

(decomp.); *phenazine* derivative, $C_{23}H_{23}O_2N_3$, m.p. 175—180° (decomp.); *p*-nitrophenylosazone, decomp. 267—268°; *triazine* derivative, $C_{18}H_{20}O_3N_4$, decomp. 238°; *dioxime*, m.p. 257°, converted by $13N-NH_3$ at 170° into the *furazan*, $C_{17}H_{19}O_3N_3$, m.p. 115—120° (decomp.). Oxidation of (IV) by $KMnO_4$ in $COMe_2$ containing Na_2CO_3 gives the *acid* (V), m.p. 222—223°, which does not react with $p-NO_2 \cdot C_6H_4 \cdot NH \cdot NH_2$ and gives a resinous *Me_2* ester when treated with CH_2N_2 , the *acid* (VI), m.p. 119—120° (*p*-nitrophenylhydrazone,



decomp. 125—127°; *Me_2* ester), which gives a distinct CHI_3 reaction when heated with I and KOH, *m*-methoxyphthalic anhydride, and an *acid* (VII), decomp. 261—262° and, after-resolidification, m.p. 240—241° (*Me_2* ester, m.p. 152—153°), which gives the fluorescein and phenolphthalein reactions of *o*-dicarboxylic acids. The *Ag* salt of (VII) decomposes at about 270° into CO_2 and 6-methoxy-2-methyldihydroisocarbostyryl, m.p. 50—51°, dehydrogenated by Pd-asbestos at 240—260° to 6-methoxy-2-methylisocarbostyryl, m.p. 96—98°, identical with the synthetic compounds. The following revised data are recorded: 2-nitro-4-acet-toluidide, m.p. 144°; 2:3-dinitro-4-acet-toluidide, m.p. 170—171°, and *p*-toluidine, m.p. 118—120°; 2:3-dinitrotoluene, m.p. 59—60°; 2-nitro-*m*-toluidine, m.p. 105—106°; 3-bromo-2-nitrotoluene, m.p. 28—29°; 3-bromo-*o*-toluidine, b.p. 105—107°/2—3 mm. (*Ac* derivative, m.p. 157—158°).

H. W.

Crystallisation of ecgonine silicotungstate. (Cinematographic recording.) R. HAZARD, J. COMANDON, and P. DE FONBRUNE (Compt. rend., 1937, 205, 922—924).—The freshly pptd. silicotungstate is amorphous; on keeping the mother-liquor deposits needle crystals, the amorphous form dissolving as formation of these proceeds. A small quantity of a third cryst. form is also produced, but is converted into the needle crystals by a similar process.

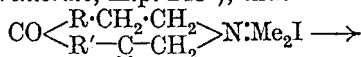
A. J. E. W.

Strychnos alkaloids. XCVI. 9-Monohydroxybrucine, the analogue of ψ -strychnine. H. LEUCHS and K. TESSMAR (Ber., 1937, 70, [B], 2369—2373; cf. A., 1937, 435).—Brucine is very slowly converted by air in presence of $CuSO_4 \cdot NH_3 \cdot H_2O$ into 9-monohydroxybrucine (ψ -brucine), $C_{23}H_{26}O_5N_2$ (I), m.p. 258—263° when crystallised from $COMe_2$ or $AcOH$, m.p. 268° when pptd. by NH_3 from hot solution, $[\alpha]_D^{20} -100^\circ/d$ in $CHCl_3$, obtained more rapidly and in much better yield by oxidation in presence of Fehling's solution (under these conditions strychnine is rapidly attacked but the product is difficult to purify). (I) gives a *perchlorate*, decomp. 220—240°, and a (?) *Me ether*, m.p. about 100°. Brucine amine oxide (*perchlorate*, m.p. 210° (decomp.)), $[\alpha]_D^{20} 0^\circ$ in H_2O or H_2O-OMe_2 , reduced by SO_2 to brucine, is obtained as by-product of the prep. of (I). $PhCHO$, (I), and $NaOMe$ in boiling $MeOH$ afford *benzylidene-ψ-brucine*, m.p. 165° (decomp.) after softening at 150°. Strongly laevorotatory *N-nitroso-*

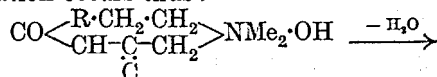
sec-ψ-brucine, m.p. 248° (decomp.), is obtained from (I), $NaNO_2$, and dil. HCl at 0°. (I) is reduced by Zn and HCl to brucine, catalytically (PtO_2 in 50% $AcOH$) to *dihydro-ψ-brucine*, m.p. 258—260° (decomp.), $[\alpha]_D^{20} +29^\circ/d$ in $CHCl_3$ free from $EtOH$ (*perchlorate*; *Me ether*, m.p. 118° (decomp.)), $[\alpha]_D^{20} +83^\circ/d$ in $CHCl_3$, also $+1MeOH$). *N-Nitrosodihydro-sec-ψ-brucine* has m.p. (indef.) 160—190° to a brown resin or m.p. 160—175° (decomp.) after being dried at 100°.

H. W.

Strychnos alkaloids. XCVII. Methylations in the series of ψ - or 9-monohydroxy-strychnine and fission of the sixth and seventh rings in the strychnine molecule. H. LEUCHS (Ber., 1937, 70, [B], 2455—2462).—The product of the action of MeI on ψ -strychnine *Me ether* (I) is the methiodide of the *N-Mc* base $C_{23}H_{27}O_3N_2I$ and therefore has the composition $C_{23}H_{27}O_3N_2I$ (cf. Leuchs, A., 1937, II, 435; Robinson and Blount, A., 1932, 1147). The base is hot, however, an intermediate since it does not add MeI at 37°. Probably the methiodide of the ether, $:C(OMe):N:MeI$, is first produced and then passes partly with migration of Me into the *N-Me_2* salt. The non-isomerised portion is ultimately hydrolysed and the OH imparts H to N so that the hydriodide of the *NMc* base results. This is converted by Me_2SO_4 into the quaternary salt, which is separated as the *perchlorate*, m.p. 285—293° (decomp.). The same salt is obtained from $C_{23}H_{27}O_3N_2I$ and $HClO_4$, thereby establishing its true nature. The migration of Me causes rupture of a ring linking in the strychnine mol. and union of two N rings one of which is five-membered and the other five-, six-, or seven-membered to a large ring. Certain valency relationships between *NMe* and *CO* appear to be retained which hinder the detection of the ketone. Reaction with semicarbazide or Clemmensen reduction could not be effected with any member of the series. In attempts to open the large ring the methoperchlorate of the base $C_{22}H_{24}O_5N_2$ is shown to pass by catalytic hydrogenation (PtO_2 in H_2O) mainly into the corresponding H_2 -derivative, m.p. 150—200°, whilst the methiodide gives small amounts of a *base*, $C_{22}H_{28}O_5N_2$, m.p. 193° (vac.) after softening, and the *methiodide*, $C_{22}H_{26}O_3N_2MeI$, m.p. (anhyd.) 215—217°. Reduction of either salt by $Na-Hg$ gives the *base*, $C_{23}H_{28}O_3N_2$, m.p. 170—172° (vac.) after softening at 165° (*perchlorate*, m.p. 243°), thus



$C:CMc \cdot R' \cdot CO \cdot R \cdot CH_2 \cdot CH_2 \cdot NMc_2 \cdot HI$. The Hofmann degradation occurs thus:



$OMe \cdot C \begin{array}{c} \text{R} \cdot CH_2 \cdot CH_2 \\ \diagup \quad \diagdown \\ C - C - CH_2 \\ | \\ C \end{array} NMe$, the *product* having m.p.

188—190° (vac.).

(I) is transformed by $PhCHO$ and 40% KOH in boiling $MeOH$ into the benzylidene derivative, m.p. 153°, and by excess of MeI at room temp. into the *methiodide*, m.p. 267° (decomp.) after softening. Hydrogenation (PtO_2) of the latter gives the *base*, $C_{24}H_{32}O_3N_2$, m.p. 189—190° (vac.) [*hydriodide*, m.p.

260—268° (decomp.); *perchlorate*, m.p. 240—246°; *methiodide* (II), m.p. 295° (vac.; decomp.). Treatment of the methiodide, $C_{23}H_{26}O_3N_2MeI$, with NaOMe in boiling MeOH gives an *isomeride*, m.p. 285—293° (decomp.), reduced by Na-Hg to the amorphous base, $C_{24}H_{30}O_3N_2$ (*perchlorate*, decomp. 135° after softening at 130°). H. W.

Strychnine and brucine. IX. R. CIUSA and V. AMORUSO (Gazzetta, 1937, 67, 723—727).—*isoStrychnine* [in the prep. of which new forms (+H₂O), m.p. 229°, and (+2H₂O), tabular, m.p. 219—222°, are obtained] with dil. HBr yields a *hydrobromide*, which with Br-H₂O gives, after treatment with aq. NH₃, *bromoisostrychnine* (I) (+CHCl₃), m.p. 140°, [α] 0° [*hydrobromide* (II) (+H₂O), m.p. 130°; Bz derivative, m.p. 162°, giving a *hydrochloride* (+H₂O), m.p. 180°]. With Br-AcOH, (II) forms *bromoisostrychnine perbromide*, decomposed by EtOH to a substance, $C_{23}H_{28}O_3N_2Br_4$. The lethal doses of (I) to the frog and the rabbit are 0.033 g. and 0.053 g. per kg., respectively. E. W. W.

Aconitum alkaloids. XII. Oxidation of Aconitum alkaloids with nitric acid. H. SUGINOME (Annalen, 1937, 533, 172—182).—Oxidation of mesaconitine, aconitine, or oxonitine (I) by HNO₃ (d 1.43) according to Brady (J.C.S., 1913, 103, 1821) gives in all cases *nitronitrosoaconitic acid* (II), $C_{18}H_{14}(OMe)_3(OH)(OAc)(OBz)(N\cdot NO)(NO_2)(CO_2H)$, decomp. 282°, [α]_D²⁰ -33.2° in EtOAc. The physical properties of the acid vary somewhat according to the source [the highest yields and purest products are derived from (I)] but all specimens are converted by AcCl into *acetyl nitroaconitic acid*, $C_{35}H_{38}O_{14}N_2$, m.p. 218—219°, [α]_D²⁰ -15.0° in EtOAc, which requires 5 mols. of alkali for hydrolysis whereas the initial material requires 3 mols. Model experiments (to be described later) show that NO₂ in (II) is attached to N. Hydrolysis of (II) with Ba(OH)₂ in EtOH affords *nitronitrosoaconic acid*, $C_{29}H_{27}O_{11}N_3$, decomp. 298°, [α]_D²⁰ -36.6° in COMe₂, which gives a well-cryst. yellow Ba salt. Lawson's acid, $C_{31}H_{35}O_{13}N_3$, m.p. 268°, appears to be identical with (II) (cf. A., 1936, 351). It seems certain that (II) does not contain a tetrahydroisoquinoline nucleus. AcCl converts (I) into *triacetyl oxonitine*, m.p. 176—178°, whence (I) contains 3 OH; the last O gained during oxidation is very probably present as CO in juxtaposition to NH, thus accounting for the neutral reaction of (I). The formula of (I) is therefore $C_{18}H_{17}(OMe)_4(OH)_3(OAc)(OBz)(NH)(CO)$.

H. W.

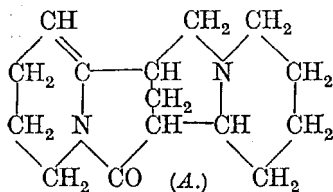
Aconitum alkaloids. XIII. New preparation of oxonine and pyroxonine. K. TAMURA (Annalen, 1937, 533, 183—196).—*Oxonine penta-acetate* (I), decomp. 246°, [α]_D²⁰ -77.09° in CHCl₃, is obtained by the oxidation of aconine penta-acetate or mesaconine penta-acetate with KMnO₄ in COMe₂ or by the action of AcCl on oxonine (II) at room temp. The 5 OH in aconine (III) and (II) must therefore be identical and, since the presence of :CO cannot be detected and that of an O bridge is improbable, it appears that the newly-introduced O exists in :CO·NH₂. Oxonine is most conveniently made by transforming jesa-

aconitine triacetate, decomp. 232° (*aurichloride*, decomp. 221°); this is oxidised by KMnO₄ in COMe₂ to *jesaconitine triacetate* (+2H₂O), m.p. 177° and, after re-solidification, m.p. 235° (decomp.), [α]_D^{17.8} -41.45° in CHCl₃, or, anhyd., decomp. 235°, which is hydrolysed to (II). Mesaconitine triacetate is similarly oxidised to *oxonitine triacetate* (+7H₂O), m.p. 178° and, after re-solidification, decomp. 235°, [α]_D^{17.9} -50.80° in CHCl₃, or, anhyd., decomp. 233°. Acetylation of (III) is effected with AcCl at room temp. during 10—14 days, or at the b.p. of Et₂O or CS₂ for 5 or 2 days. Boiling AcCl is very unsuitable. Pyromesaconitine hydrobromide is transformed by AcCl at 36° into *pyromesaconitine diacetate* (IV) $C_{34}H_{45}O_{11}N$, m.p. 202—205°, [α]_D¹⁹ -101.86° in CHCl₃ (*perchlorate*, decomp. 304°; *aurichloride*, decomp. 225°), and an isomeric base (*perchlorate*, m.p. 193° after softening at 187°; *aurichloride*, decomp. 208°). KMnO₄ oxidises (IV) in COMe₂ to *pyroxonitine diacetate*, decomp. 170° after softening at 160°, [α]_D²⁰ -115.49° in CHCl₃ (identical with that obtained from the base and AcCl at 36°), hydrolysed by 0.25N-Ba(OH)₂ in EtOH to pyroxinine, $C_{23}H_{33}O_9N$, 0.5EtOH, H₂O, decomp. 264°. This with AcCl at 36° affords pyroxinine triacetate, $C_{29}H_{39}O_{12}N$, 1.5H₂O, m.p. 165° (*hydrochloride*, m.p. 158° and, after re-solidification, m.p. 219°; *aurichloride*). H. W.

Alkaloids of Aconitum napellus. W. FREUDENBERG and E. F. ROGERS (J. Amer. Chem. Soc., 1937, 59, 2572—2575).—The residual bases from the tubers of *A. napellus* contain *napelline*, $C_{22}H_{33}O_3N$, cryst. [*hydrobromide*, m.p. 229° (decomp. from 200°), [α]_D²³ -42.7° in H₂O; *hydrochloride*, m.p. 220—222° (decomp.), [α]_D²⁸ -93.9° in H₂O; *hydriodide*, m.p. 181—185° (decomp.)], *neoline*, $C_{24}H_{41}O_6N$, m.p. 153—154°, [α]_D²⁸ +9.7° in EtOH [*hydrobromide*, m.p. 215° (decomp.), [α]_D²³ +2.1° in H₂O; *hydrochloride*, decomp. 178—180°], with traces of *l*-ephedrine and *l*-sparteine. R. S. C.

Alkaloids of Anabasis aphylla. XIV. Structure of aphylline and aphyllidine. A. ORÉKHOV (J. Gen. Chem. Russ., 1937, 7, 2048—2062).—Aphyllidine (I) (A., 1932, 405), purified via the *perchlorate*, m.p. 210—212°, [α]_D +15° in MeOH, has m.p. 112—113°, and [α]_D +6.5° in MeOH; the higher [α] and lower m.p. previously reported were due to contamination with an unknown alkaloid, m.p. 162—164°, [α]_D +54.5° in MeOH. In light petroleum (I) and Br yield the *hydrobromide*, m.p. 210°, of *bromoaphyllidine* (II), m.p. 150—152° (*perchlorate*, m.p. 235°), attempted hydrogenation, reduction, and hydrolysis of which were unsuccessful. De-N-methylaphyllidine (III) is brominated in light petroleum to a Br₁-derivative, b.p. 190—193°/17 mm. (*perchlorate*, m.p. 180—183°), also prepared from the *methiodide*, m.p. 114—120°, of (II) and Ag₂O. In EtOH and HCl at 100° (I) gives *Et aphyllidate*, m.p. 210—212° (*picrate*, +COMe₂, m.p. 208—210°), showing that ring fission takes place. Hydrogenation of (I) (Pt catalyst) gives aphylline, which is thus 5:6-dihydroaphyllidine. Reduction of (I) in 50% H₂SO₄ with Pb electrodes gives *d*-sparteine. The *methiodide*, m.p. 121—122°, of de-N-dimethylaphyllidine, b.p. 240—242°/7 mm. (*perchlorate*, m.p.

180—182°), and Ag_2O in MeOH give hemiaphyllidylene, $\text{C}_{15}\text{H}_{19}\text{ON}$. In N-HCl (III) and H_2 (Pt catalyst) yield dihydrode-*N*-methylaphyllidine, m.p. 118—120° (methiodide, m.p. 234—235°), with which Ag_2O gives dihydrode-*N*-dimethylaphyllidine, b.p.



218—220°/5 mm. (*perchlorate*, m.p. 209—210°), the methiodide, m.p. 195°, of which gives dihydrohemiaphyllidylene, b.p. 206—207°/8 mm., with Ag_2O in MeOH; the compounds thus obtained are identical with, and of higher purity than, those obtained analogously from aphylline (*loc. cit.*). The structure of (I) is regarded as being A.

R. T.

Action of lead tetrachloride on primary and secondary halogenated arsines, and on tertiary arsines. G. J. BURROWS and A. LENCH (J. Proc. Roy. Soc. New South Wales, 1937, 70, 294—299).— PbCl_4 at -5° in CHCl_3 converts AsPhMe_2 into $\text{AsClPhMe}_2\cdot\text{OH}$, AsPh_2Me into *diphenylmethyl*-, m.p. 132°, and AsPhMeEt into *phenylmethylethyl*-arsine dichloride, m.p. 83°, (the last two are also obtained from the arsine and Cl_2). Similarly *o*- (but not *p*-) $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsCl}_2$ gives $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsCl}_4$, whilst *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsMeCl}$ yields *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsMeCl}(\text{OH})_2$, converted by H_2O into *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsMeO}\cdot\text{OH}$, or by PbCl_4 in CHCl_3 above 10° into *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsO}(\text{OH})_2$. No additive compounds of PbCl_4 with arsines could be isolated.

A. Li.

Dihydroxydiphenylarsonium chloride. G. J. BURROWS and A. LENCH (J. Proc. Roy. Soc. New South Wales, 1937, 70, 300—301).—Treatment of $(\text{AsPh}_2)_2\text{O}$ in CHCl_3 with dry Cl_2 yields $\text{AsPh}_2\text{Cl}(\text{OH})_2$, m.p. 128°, and not the oxychloride $(\text{AsPh}_2\text{Cl}_2)_2\text{O}$ of La Coste and Michaelis (A., 1880, 396).

A. Li.

Derivatives of diphenylmethylarsine. G. J. BURROWS and A. LENCH (J. Proc. Roy. Soc. New South Wales, 1937, 70, 437—439).— AsPh_2Me with Br in CCl_4 gives *diphenylmethylarsine dibromide*, m.p. 116° (decomp.), or *tetrabromide*, m.p. 63—64°; with I in CHCl_3 it gives the *di-iodide*, m.p. 104° (decomp.). AsPh_2MeO and hot EtOH-HCl yield *hydroxydiphenylmethylarsonium chloride*, m.p. 147°.

A. Li.

Mercuration and arsenation of benzothienone [2-benzoylthiophen]. A. W. WEITKAMP and C. S. HAMILTON (J. Amer. Chem. Soc., 1937, 59, 2699—2702).—2-Benzoylthiophen with $\text{Hg}(\text{OAc})_2$ and HgCl_2 in hot AcOH give 2-benzoyl-5-chloromercurithiophen (I), m.p. 242°; $\text{Hg}(\text{OAc})_2$ alone at 100° gives a 1:1 mol. compound, m.p. 202°, of 2-benzoyl-5-acetoxymercuri- (not isolated) and -4:5-diacetoxymercuri-thiophen (II), the latter product being prepared from the mol. compound by $\text{Hg}(\text{OAc})_2$ in $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OMe}$. With KI_3 (I) gives 2-iodo-5-benzoylthiophen, m.p. 129.5—130° (3- NO_2 -derivative, m.p. 168°), also obtained from 2-iodothiophen, BzCl , and SnCl_4 in C_6H_6 . Thiophen, $\text{C}_6\text{H}_4\text{I}\cdot\text{COCl}$, and SnCl_4 yield 2-*o*-, m.p. 61°, -*m*-, m.p. 48°, and -*p*-iodobenzoylthiophen, m.p. 106.5°, which yield 5-*HgCl* derivatives, m.p. 225°, 252°, and 285° (decomp.), respectively; these

derivatives with KI_3 yield 2-iodo-5-*o*-, a glass (3- NO_2 -derivative, m.p. 138—139°), -*m*-, m.p. 109°, and -*p*-iodobenzoylthiophen, m.p. 153°. With KI_3 (II) gives 2:3-di-iodo-5-benzoylthiophen, m.p. 80—90°. With KBr_3 (I) and (II) give 2-bromo-, m.p. 76°, and 2:3-dibromo-5-benzoylthiophen, m.p. 80°, respectively. With AsCl_3 (I) gives 2-benzoylthienyl-5-dichloroarsine, m.p. 113°, and thence 2-benzoylthienyl-5-arsinous oxide. Either of these with $\text{NaOH-H}_2\text{O}_2$ gives 2-benzoylthienyl-5-arsinic acid, m.p. 360° (decomp.; 1 H_2O lost at 140°).

R. S. C.

Action of Grignard's reagent on silicon tetrafluoride. Fluorotriphenylmonosilane. G. V. MEDOX and N. Z. KOTELKOV (J. Gen. Chem. Russ., 1937, 7, 2007—2008).— SiF_4 and MgPhBr in Et_2O yield fluorotriphenylsilane, m.p. 64°.

R. T.

Complex compounds obtained from *p*-tolylstibine dichloride and *p*-tolyl diazonium chloride. II. A. B. BRUKER and E. S. MACHLIS (J. Gen. Chem. Russ., 1937, 7, 1880—1884).—*p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\text{Cl}$ (I) and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SbCl}_2$ in AcOH yield a 1:1 compound, m.p. 90—92° (decomp.), converted by boiling 25% HCl into (*p*- $\text{C}_6\text{H}_4\text{Me}$) $_2\text{SbCl}_3$, m.p. 155° (lit. 143°). In presence of excess of (I) a 2:1 compound, m.p. 108—110°, is obtained, and this, when boiled with 25% HCl , gives (*p*- $\text{C}_6\text{H}_4\text{Me}$) $_2$, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SbCl}_4$, and the double salt *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SbCl}_4\cdot\text{NH}_4\text{Cl}$, not melting at 200° , and converted into *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{Sb}(\text{OH})_2$ by shaking with H_2O .

R. T.

Benzylstibines and their derivatives. I. TZUKERVANIK and D. SMIRNOV (J. Gen. Chem. Russ., 1937, 7, 1527—1531).— CH_2PhCl , Mg, and SbCl_3 in Et_2O yield tribenzylstibine oxide, together with dibenzyl, PhCHO , and Sb_2O_3 . The oxide is converted by HCl or HBr into tribenzylstibine dichloride, m.p. 100—101°, or dibromide, m.p. 107—109°. When the Grignard reaction is conducted with strict exclusion of air, the product is tribenzylstibine, m.p. 85—90°, which with excess of SbCl_3 gives dibenzylchlorostibine dichloride, m.p. 157—158°. This is converted by aq. Na_2CO_3 into dibenzylstibine oxide, $[(\text{CH}_2\text{Ph})_2\text{SbO}]_2$, which with HBr gives dibenzylbromostibine dibromide, m.p. 150—151° (decomp.).

R. T.

Organic thallium derivatives. VII. Synthesis of organic thallium derivatives with the simpler substituents in the benzene ring. N. N. MELNIKOVA and M. S. ROKITSKAJA (J. Gen. Chem. Russ., 1937, 7, 1472—1477).—The compounds $\text{TlR}_3\cdot\text{X}$ are prepared from RX , Mg, and TlX_3 in Et_2O : $\text{R} = m\text{-tolyl}$, $\text{X} = \text{Cl}$, m.p. 235°; $\text{R} = m\text{-tolyl}$, $\text{X} = \text{Br}$, m.p. 242°. ($\text{OAc}\cdot\text{C}_6\text{H}_4$) $_2\text{Hg}$ in boiling EtOH and TlBr_3 yield *di-p*-acetoxyphenylthallium bromide. TlBr_3 and *p*- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{B}(\text{OH})_2$ in boiling H_2O yield *di-p*-carboxyphenylthallium bromide (I), m.p. $>260^\circ$. $\text{C}_6\text{H}_4\text{PhBr}$ in Et_2O , Mg, and $\text{OBu}^t\cdot\text{B}(\text{OH})_2$ yield diphenylthalluric acid, m.p. 185—190°, which with TiCl_3 or TlBr_3 in boiling H_2O gives diphenylthallium chloride, decomp. at 240—245°, or bromide, not melting at 305° ; the last with excess of TlBr_3 gives diphenylthallium dibromide (II), m.p. 185° (decomp.). ($\text{NO}_2\cdot\text{C}_6\text{H}_4$) $_2\text{TiCl}$, m.p. 245° (decomp.), ($\text{NO}_2\cdot\text{C}_6\text{H}_4$) $_2\text{TlBr}$, m.p. 238° (decomp.), $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{TiCl}_2$, m.p. 217° (decomp.), and

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{TiBr}_2$, m.p. 178° (decomp.), are prepared analogously to (I) and (II). R. T.

How to determine structural formulæ for proteins. W. D. BANCROFT and H. F. BROWNING (J. Physical Chem., 1937, 41, 1163—1170).—For studying the constitution of proteins a scheme is proposed, based on the determination of different forms of N (total, "stoichiometric," and NH_3) in fractional hydrolysates, and in degradation products obtained in different ways. Dil. H_2SO_4 is preferred to HCl for hydrolysis. Some preliminary results for casein are recorded. F. L. U.

Relation between "fibrous" and "globular" proteins. W. T. ASTBURY (Nature, 1937, 140, 968—969).—Accumulating X-ray evidence for the view that fibrous and globular proteins are constructed on a common plan is summarised. The chemical data of Bergmann and Niemann (A., 1937, III, 168) indicate a similar view. L. S. T.

Structure of the protein molecule. F. HALLE (Kolloid-Z., 1937, 81, 334—349).—A review.

Accidents in destruction of organic and biological substances with perchloric acid. E. KAPANE (Z. anal. Chem., 1937, 111, 14—17; cf. A., 1932, 71).—The action of HClO_4 on org. substances may become explosive in the absence of a diluent, such as H_2SO_4 or excess of HClO_4 . J. S. A.

Determination of carbon and hydrogen content by combustion. M. W. RENOLL, T. MIDGLEY, jun., and A. L. HENNE (Ind. Eng. Chem. [Anal.], 1937, 9, 566—567).—Combustion of 0.1—0.2 g. in an electrically heated all-glass apparatus using an air current (cf. Smith *et al.*, A., 1933, 641) gives C and H correct to 0.01%. The at. wt. of C must be taken as 12.005. F. R. G.

Demands made on lead dioxide in micro-analysis [for carbon and hydrogen]. A. FRIEDRICH (Mikrochem., 1937, 23, 129—143).—The N liberated as NO_2 in the combustion of org. compounds varies from 5—30% in azo- or NH_2 -compounds to 50% in NO_2 - or NO-compounds, and is dependent on the rate of combustion and the catalyst used. The optimum amount of PbO_2 for use in micro-combustion tubes is discussed. J. S. A.

Micro-determination of sulphate solutions.—See A., I, 44.

Determination of deuterium in organic compounds. A. S. KESTON, D. RITTENBERG, and R. SCHOENHEIMER (J. Biol. Chem., 1938, 122, 227—237; cf. A., 1935, 1407).—The org. compound is burnt, H_2O formed is purified, and $[\text{D}_2\text{O}]$ in this H_2O determined by two independent methods, *n* and *d* being determined. Methods and apparatus are described. J. N. A.

Direct micro-determination of oxygen in organic substances by hydrogenation. Analysis of pure volatile compounds containing carbon, hydrogen, and relatively low percentages of oxygen. W. R. KIRNER (Ind. Eng. Chem. [Anal.], 1937, 9, 535—539).—A procedure similar to that of Hennig (A., 1936, 872; see also Unterzaucher and Bürger, A., 1937, II, 358) is described. H_2O formed

is absorbed by anhyd. CaSO_4 . The necessity of using an empirical blank val. is emphasised [cf. Lindner and Wirth, *ibid.* (1937)]. When the method is applied to sucrose the vals. are consistently low.

F. R. G.

Micro-determination of oxygen. (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1937, 46, 428—433).—A more detailed account of the method already described (A., 1937, II, 436). Halogens in N-free compounds are determined by hydrogenation to the halogeno-acids, which are titrated. J. D. R.

Determination of nitrogen in highly nitrated substances by the ter Meulen method. P. M. HEERTJES (Chem. Weekblad, 1937, 34, 827).—Trustworthy results can be obtained with highly nitrated substances by using 1 g. of Ni containing 10% of ThO_2 per 10 mg. of sample, adding a few drops of an appropriate solvent (*e.g.*, COMe_2) to spread the substance throughout the catalyst mass, and heating at 100° for 1 hr. before heating to a higher temp. in order to disengage NH_3 . Results for di- and trinitropyrocatechol ethylene ethers are discussed. S. C.

Halogenorganimetry. Determination of halogens in organic substances. J. A. SANCHEZ (J. Pharm. Chim., 1938, [viii], 27, 5—18; cf. A., 1936, 1528).—The substance (0.02 g.) is heated with KMnO_4 and powdered pumice and an aq. solution of the powder is treated with H_2O_2 . I is determined as IO_3^- . For Cl, the neutralised filtrate is treated with CaCO_3 and the Cl determined titrimetrically. When the substance contains Br, the acidified solution of the fusion mixture is treated with MnO_2 and the Br liberated distilled into a solution of an alkali iodide; the I liberated is titrated. The method is widely applicable with an error of <1%. J. L. D.

Determination of micro-quantities of iodine.—See A., I, 44.

Determination of acetyl, especially in O-acetyl compounds. E. P. CLARK (Ind. Eng. Chem. [Anal.], 1937, 9, 539).—If in the method described previously (A., 1937, II, 40) the reaction mixture is distilled at a rate such that it is conc. to approx. 15 c.c. during the collection of the 50 c.c. of distillate instead of steam-distillation at const. vol., all the AcOH is found in the distillate. L. S. T.

Diazometric analysis of dienes, and its applications. A. P. TERENTIEV (Prom. Org. Chim., 1937, 4, 535—542).—The method is applicable to determination of cyclopentadiene, $(\text{CH}_2\cdot\text{CMe})_2$, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$, $\text{CHMe}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$, $\text{CH}_2\cdot\text{CCl}\cdot\text{CH}\cdot\text{CH}_2$, and pyrrole. R. T.

Micro-acetyl determination. Titration of weak bases. F. VON VIDITZ (Mikrochim. Acta, 1937, 1, 326—337).—A simplified form of apparatus is described. Phosphotungstic acid is used in place of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ as a hydrolysing agent, and dioxan as a solvent for Ac compounds of low solubility. The titration of weak acids by weak bases is discussed, and $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ is recommended for the titration of AcOH and other weak acids. The method gives satisfactory results with 0.7 mg. of phenacetin or 0.4 mg. of cellobiose octa-acetate. The possibility of a new

acidimetric method for the determination of fructose is pointed out. L. S. T.

Micro- and submicro-determination and identification of ethyl alcohol. II. Submicro-determination. III. Identification. M. NICLOUX (Ann. Ferment., 1936, 1, 513—529, 530—540; Chem. Zentr., 1936, i, 4189—4190).—II. A modification of the $K_2Cr_2O_7$ process is described, applicable to 0.1—0.5 mg. of $EtOH$ (e.g., in blood).

III. The oxidation of $EtOH$ to $AcOH$ requires the theoretical amount of $K_2Cr_2O_7$, whereas $PrOH$, Bu^oOH , and Bu^sOH require 1.21—1.26, 1.27, and 1.24—1.42 times the theoretical $K_2Cr_2O_7$, according to temp., and yield < the theoretical amount of the corresponding acids. J. S. A.

Rapid determination of primary and secondary alcohols by phthalisation in warm pyridine, and identification of the alcohols as their acid phthalates. S. SABETAY and Y. R. NAVES (Ann. Chim. Analyt., 1937, [iii], 19, 285—289; cf. A., 1937, II, 132).—Primary alcohols with an excess (2—4 times) of $o-C_6H_4(CO)_2O$ (I) in C_5H_5N (100° ; 1 hr.) afford esters quantitatively; the extent of combination is determined titrimetrically after hydrolysis of excess of (I) with hot H_2O . Some *sec.* alcohols react similarly, but many do not as they are dehydrated or their groups exert steric influences on the phthalyl residue. Easily hydrolysed esters are determined after reaction at room temp. Many practical points dealing with the separation of these products are described. J. L. D.

Determination of glycerol and ethylene glycol in dilute aqueous solution. A. G. HOVEY and T. S. HODGINS (Ind. Eng. Chem. [Anal.], 1937, 9, 509—511).—The colour reactions of phenols in acid, neutral, and alkaline solution with glycerol (I) and $(CH_2OH)_2$ (II) show that (I) in presence of (II) is best detected by pyrocatechol and H_2SO_4 , which gives a blood-orange colour at 140 — 145° . The colours given with the reagent by several polyhydric alcohols are recorded. The test fails in presence of aldehydes but may be used to detect acraldehyde (flocculent purple ppt.) in presence of (I).

F. R. G.

Rapid hydrolysis of esters by potassium hydroxide in diethylene glycol. C. E. REDEMANN and H. J. LUCAS (Ind. Eng. Chem. [Anal.], 1937, 9, 521—522).—Sap. vals. of esters and oils are determined by hydrolysis with $N-KOH$ in $(OH-C_2H_4)_2O$ (I) at suitable temp. up to 130° followed by titration with $0.5N-HCl$. Procedure for identification of esters using KOH in (I) allows ready separation of the alcohol. F. R. G.

Polarimetric titration of hydroxy-acids. F. GÓRSKI (Bull. Acad. Polonaise, 1937, A, 239—243).—Optically active OH -acids, e.g., tartaric and malic acid, are determined by adding the enantiomorph to an aq. solution of the acid and NH_4 molybdate (I) until α is 0° . The method is accurate because the low $[\alpha]$ of the acid is changed by (I) to very high $[\alpha]$ of opposite sign. R. S. C.

Recognition and determination of traces of formaldehyde. J. M. HAMBERSIN (Bull. Soc. chim.

Belg., 1937, 46, 519—524).—With $\beta-C_{10}H_7-OH$ and H_2SO_4 , CH_2O gives a pink colour which on boiling yields a pink ppt. The above pink colour serves for the recognition of, and in absence of other aldehydes (e.g., $MeCHO$) for the colorimetric determination of, CH_2O by comparison with freshly prepared standards. Gravimetric determination is carried out by weighing the ppt. formed on boiling. J. D. R.

Use of drop analysis for investigation of medicaments. II. New test for amines, with especial consideration of *p*-phenylenediamine, and a new reaction for proteins. O. FRÉHDE and L. GOLDSCHMIDT (Mikrochim. Acta, 1937, 1, 338—353; cf. A., 1937, II, 476).—The formation of coloured Schiff's bases with furaldehyde (I) or $p-NMe_2-C_6H_4-CHO$ (II) in glacial $AcOH$ provides a micro-test for primary and *sec.* amines. (I) gives mainly red to violet, and (II) orange-yellow to red, products. Colours and limiting sensitivities for numerous amines are tabulated. NH_2 -acids, but not *tert.* amines, also react. The tests can be used with advantage in detecting adulteration of drugs and remedies; an example in which the adulterant was $p-C_6H_4(NH_2)_2$ is quoted. Primary aromatic amines can be detected by the formation of brown, red, or violet condensation products with a saturated $AcOH$ solution of 5-nitroso-8-hydroxyquinoline or, with less sensitivity, with a 10% glacial $AcOH$ solution of $p-NMe_2-C_6H_4-NO$. Condensed-ring systems such as $C_{10}H_7-NH_2$ react best. Primary and *sec.* amines also yield coloured condensation products with a saturated solution of chloranil in dioxan; sensitivities and colours are tabulated. NH_2 -acids and proteins do not react, but phenols interfere by giving red to violet colours. Free inorg. and org. bases must first be neutralised with $AcOH$. Aldehydes and carbohydrates are without effect. This test can be used on paper. (II) in glacial $AcOH$ provides a test for proteins in presence of conc. HCl .

L. S. T.

Effect of pyruvic acid on the determination of cystine and cysteine. M. X. SULLIVAN and W. C. HESS (J. Biol. Chem., 1938, 122, 11—17).— $AcCO_2H$ has no effect on the colorimetric determination of cystine; in conc. solution it rapidly forms a complex with cysteine at pH 6, which is decomposed by boiling for 10 min. with 2% HCl , yielding quant. vals. by the colorimetric method. P. G. M.

Chemistry of Jaffé's reaction for creatinine. A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1937, 70, 357—363).—Creatinine (1 mol.) in $NaOH-EtOH$ and alcoholic picric acid (2 mol.) give an explosive red compound containing creatinine, picric acid, and $NaOH$ (1:1:2 mol.), which is converted by HCl into the red isomeride of creatinine picrate, and is probably the red compound of Jaffé's reaction. A. LI.

Determination of phenanthrene. M. A. ILJINSKI and P. B. ROSCHAL (Compt. rend. Acad. Sci. U.R.S.S., 1937, 17, 120—124).—Determination of phenanthrene (I) (in mixtures with anthracene etc.) by prep., in xylene, of its picrate (which is weighed, and the amount in solution calc., after a second pptn. using the same mother-liquor) is not satisfactory.

Oxidation of phenanthraquinone (II) by CrO_3 varies with the amount of AcOH , H_2O , or H_2SO_4 present. Separation of (II) through its H sulphite compound is not complete, but (II) can be separated fairly well from anthraquinone by means of its oxime. The use of this to determine (I) will depend on a quant. method of oxidising (I) to (II).
E. W. W.

Microchemical detection of some phenols. E. EEGRIWE (Mikrochem., 1937, 23, 173—175).— PhOH and *o*-cresol give rose-pink colorations when warmed with $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and 63% H_2SO_4 at 65° . Other phenols give less sp. colorations or do not react. Orcinol gives a green fluorescence when treated with 1 : 2 : 4- $\text{CHO}\cdot\text{C}_6\text{H}_3(\text{OH})_2$ in HCl and then made alkaline. Other phenols do not react or give non-sp. fluorescence.
J. S. A.

Determination of nitrogen in picric acid with hydrogen peroxide in strongly alkaline solution. A. LECCO and L. LILIĆ (Bull. Soc. Chim. Yougoslav., 1937, 8, 77—82).—Utz's method gives results 2.5% too low with picric acid. Results for other NO_2 -compounds are also tabulated.
F. L. U.

Use of polarographs in determining ketones. G. T. BORCHERT, V. W. MELOCHE, and H. ADKINS (J. Amer. Chem. Soc., 1937, 59, 2171—2176).—The procedure described by Winkel and Proske (A., 1937, I, 152) is applied to mixtures of COPhMe and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{COMe}$. 0.001—1 mg. may be determined by comparison with the wave heights of standard solutions, the error being <2%. Methods of measuring polarographs are compared.
F. R. G.

Spectrographic determination of 2-acetylpyrrole. S. A. SCHOU and M. TØNNESEN (Dansk Tidsskr. Farm., 1937, 11, 344—348).—2-Acetylpyrrole may be determined spectrographically by its maxima at 2810 \AA . in Et_2O , and 2880 \AA . in H_2O . In this way its partition coeffs. $\text{H}_2\text{O}/\text{Et}_2\text{O} = 0.13$ and $\text{H}_2\text{O}/\text{hexane} = 5.5$ have been measured.
M. H. M. A.

Determination of diethylnicotinamide and bisdiethylphthalamide. K. A. JACKEROTT and F. REIMERS (Dansk Tidsskr. Farm., 1937, 11, 306—314).— $o\text{-C}_6\text{H}_4(\text{CO}\cdot\text{NEt}_2)_2$, after 30 min. hydrolysis with boiling 2*N*- HCl , and $o\text{-C}_6\text{H}_4\text{N}\cdot\text{CO}\cdot\text{NEt}_2$ (I), untreated, are determined by Kjeldahl distillation and collection of the NHEt_2 in 0.1*N*- HCl . Care must be taken to avoid volatilisation of (I) and to ensure complete distillation of NHEt_2 .
M. H. M. A.

Determination of carbazole by its hydroxymethyl derivative. M. A. LJINSKI and P. B. ROSCHAL (Compt. rend. Acad. Sci. U.R.S.S., 1937, 17, 117—120).—Carbazole (I) is determined by combining it with CH_2O to *N*-hydroxymethylcarbazole, hydrolysing this by heating with H_2O , oxidising the resulting CH_2O by Na_2O_2 to HCO_2Na , and titrating excess of NaOH . The method is satisfactory either with pure (I) or in presence of phenanthrene, anthracene, indole, or acridine.
E. W. W.

Kapeller-Adler method for determining histidine.—See A., III, 151.

Action of potassium permanganate on sparteine. Effect on the determination of this alkaloid. A. GUILLAUME and (MLLE.) A. PROSCHELL (Bull. Soc. Pharmacol., 1937, 44, 475—478).—Sparteine is attacked by acidified KMnO_4 , but only if an excess of KMnO_4 is present. Bourcet and Dugué's method (*ibid.*, 1930, 37, 49) of determining sparteine is thus valid (cf. Jaretsky *et al.*, A., 1934, 708).
R. S. C.

Indirect determination of cocaine in mixtures of cocaine and novocaine. S. N. CHAKRAVARTI and M. B. ROY (Current Sci., 1937, 6, 219—220).—Novocaine (I) is determined as follows, and the cocaine (II) found by difference: an aq. solution of 2—10 mg. of mixture is treated with a slight excess of NaNO_2 in presence of a slight excess of dil. H_2SO_4 , and 5 c.c. of 10% NaOH and 1 c.c. of 1% $\beta\text{-C}_{10}\text{H}_7\text{OH}$ are added; the colour produced is matched against suitable standards. M.p. data and curve are given for mixtures of hydrochlorides of (I) and (II).
J. N. A.

Microchemical reaction for differentiating strychnine and brucine. A. MARTINI (Mikrochem., 1937, 23, 164—167).—The alkaloids are distinguishable from the characteristic habit of the ppts. given with RhCl_3 .
J. S. A.

Comparative microscopic tests of anabesine and its related compounds, its purification, and some physical constants. A. G. SOKOLOV (Mikrochem., 1937, 23, 147—148; cf. Zerbey *et al.*, A., 1937, II, 314).—Polemical. Pure anabesine is readily prepared and identified by means of its salt with H_2SiF_6 .
J. S. A.

Determination of thiol groups in proteins. R. KUHN and P. DESNUELLE (Z. physiol. Chem., 1938, 251, 14—18; cf. A., 1935, 1252; Todrick and Walker, A., 1937, III, 130).—Thiol groups (*e.g.*, in native or denatured proteins) are determined colorimetrically by treatment with freshly prepared aq. solution of porphyrindine (porphyrin acts in the same way but its colour interferes) which quantitatively dehydrogenates thiol to disulphide groups at room temp. The protein of the yellow enzyme and native ovalbumin contain no thiol groups but heat-denatured ovalbumin contains 0.58% of cysteine.
W. McC.

Determination of amino-nitrogen in insoluble proteins. H. A. RUTHERFORD, M. HARRIS, and A. L. SMITH (J. Res. Nat. Bur. Stand., 1937, 19, 467—477).—When treated with HNO_2 , proteins and other NH_2 -compounds liberate N_2 in two stages. The initial rapid stage or blank, which is due to spontaneous decomp. of HNO_2 , depends on p_{H} , the size of the blank increasing with decreasing p_{H} . The blank is decreased by approx. 80% by means of a $\text{AcOH}\text{-NaOAc}$ buffer of p_{H} 3.4—4.0. In the second stage, the rate at which N_2 is evolved decreases with increase in p_{H} . Extrapolation to zero time of the straight-line portions of time- N_2 evolved curves is considered to give vals. for the NH_2 content of proteins which are trustworthy and, for cryst. egg-albumin and collagen, compare favourably with vals. otherwise obtained.
C. R. H.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MARCH, 1938.

Valencies of carbon.—See A., I, 122.

Simplified method of writing electronic formulæ.—See A., I, 122.

Aliphatic substitution and the Walden inversion. E. D. HUGHES (Trans. Faraday Soc., 1938, 34, 202—221).—Published work is summarised and discussed. E. S. H.

Ozonation of hydrocarbons (hexane, heptane, and octanes).—See A., I, 148.

Reaction of pure hydrocarbons in presence of aluminium chloride. G. EGLOFF, E. WILSON, G. HULLA, and P. M. VAN ARSDELL (Universal Oil Products Co., Chicago, Booklet No. 212, 1937, 74 pp.).—The reactions of various hydrocarbons are reviewed. R. B. C.

Reaction mechanism for nitrating paraffin hydrocarbons. R. F. MCCLEARY and E. F. DEGERING (Ind. Eng. Chem., 1938, 30, 64—67).—A mechanism is suggested to account for all the observed products of vapour-phase nitration of paraffin hydrocarbons. Evidence is given in support of the view that free radical formation is an essential intermediate step in the reaction, oxidation of the hydrocarbon or some induced dissociation leading to the formation of these radicals, which in turn react with the HNO_3 affording nitroparaffins. The observed oxidation products may be accounted for by assuming direct oxidation of either the parent hydrocarbon or olefine shown to be formed during the reaction. F. N. W.

Nitration of *n*-pentane. H. B. HASS and J. A. PATTERSON (Ind. Eng. Chem., 1938, 30, 6769).—Vapour-phase nitration of *n*-pentane by the method previously described (A., 1936, 587) affords nitromethane (1.1) and -ethane (7.19), α -nitro-propane (13.85) and -butane (12.5), and α - (21.6), β - (20.8), and γ -nitropentane (23.0%). These findings agree with the views of McCleary and Degering (preceding abstract). F. N. W.

Polymerisation of propylene by dilute phosphoric acid. L. A. MONROE and E. R. GILLILAND (Ind. Eng. Chem., 1938, 30, 58—63).—Stepwise polymerisation of $\text{CHMe}:\text{CH}_2$ with 10—50% H_3PO_4 at 260—235°/170—410 atm. shows that the first product is the dimeride, which with more $\text{CHMe}:\text{CH}_2$ forms the trimeride and thence the tetrameride. With temp. <300° and $[\text{H}_3\text{PO}_4]$ <30%, the composition of the product (100—35% dimeride) depends solely on the extent of polymerisation of the feed; above these limits the dimeride content of the mixed polymerides is decreased with increased yield of more complex compounds. The mechanism of the reaction

is discussed in view of the fact that the observed rate of polymerisation \propto the square of the gas-phase $\text{CHMe}:\text{CH}_2$ concn., and to the first power of the acid concn. F. N. W.

Reactions of isoprene and dimethylbutadiene. G. DUPONT and C. PAQUOT (Compt. rend., 1937, 205, 805—807; cf. A., 1937, II, 27).—Isoprene (I) in EtOH with H_2 -Raney Ni in an atm. of H_2 at 0° gives a mixture of equal amounts of $\text{CMeEt}:\text{CH}_2$ and γ -methyl- Δ^2 -butene (II), but no $\text{CHPr}^2:\text{CH}_2$ as determined by the Raman spectrum. 3 H is absorbed at "complete" hydrogenation, when the Raman spectrum indicates the presence of (II) only. $\beta\gamma$ -Dimethylbutadiene (III) similarly absorbs 2 H to give 67% of $\beta\gamma$ -dimethyl- Δ^2 -butene and 33% of $\beta\gamma$ -dimethyl- Δ^3 -butene. (I) with $\text{CBz}:\text{CBz}$ in a sealed tube at 120—130° affords 1:2-dibenzoyl-4-methyl- $\Delta^{1,4}$ -cyclohexadiene, m.p. 58—59°. (III) similarly affords 1:2-dibenzoyl-4:5-dimethyl- $\Delta^{1,4}$ -cyclohexadiene, m.p. 106—107°. J. L. D.

Mechanism of polymerisation. II. Dimerisation of $\beta\gamma$ -dimethylbutadiene in presence of an acid catalyst. E. H. FARMER and R. C. PITKETHLY (J.C.S., 1938, 11—19).—With 0.1% H_2SO_4 in AcOH, $(\text{CH}_2:\text{CHMe})_2$ (I) yields 1:3:4-trimethyl-1-isopropenyl- Δ^3 -cyclohexene (II), b.p. 85°/15 mm., 202—203°/761 mm., the structure of which is proved by the following synthesis. (I) with $\text{CH}_2:\text{CMe}:\text{CO}_2\text{Me}$ yields *Me* 1:3:4-trimethyl- Δ^3 -tetrahydrobenzoate (III), b.p. 106°/19 mm., hydrolysed by NaOH-EtOH to 1:3:4-trimethyl- Δ^3 -tetrahydrobenzoic acid, m.p. 56° (anilide, m.p. 94.5°), and converted by O_3 in EtOAc into *Me* α -acetonyl- γ -acetyl- α -methylpropionate (disemicarbazone, m.p. 200°). (III) with MgMeI in Et_2O yields 1-acetyl-1:3:4-trimethyl- Δ^3 -cyclohexene (semicarbazone, m.p. 151°), 1:3:4-trimethyl- Δ^3 -cyclohexenyldimethylcarbinol (IV), b.p. 105—108°, and a liquid [probably the *Me* ether of (IV)], b.p. 68—71°. Dehydration of (IV) with KHSO_4 yields (II), which with Pt-H_2 in EtOH gives a H_2 -compound (not homogeneous), and this with Br in CS_2 gives the solid (m.p. 57°) and liquid stereoisomerides of 1:2-dibromo-1:2:4-trimethyl-4-isopropylcyclohexane. Hydrogenation of (II) with HI-P or Pt-H_2 in AcOH (poor yields) gives 1:2:4-trimethyl-4-isopropylcyclohexane, b.p. 177°, whilst with Se at 300° an oil, b.p. 160—170° (probably 3:4-dimethylcumene), is formed which is oxidised (KMnO_4 - Na_2CO_3) to trimellitic acid. Ozonolysis of (II) affords CH_2O in 70% yield, and oxidation (KMnO_4) gives a dicarbonyl compound, $\text{C}_{12}\text{H}_{20}\text{O}_2$ (disemicarbazone, m.p. 251°), which is considered to originate from a dicyclic dimeride present as impurity in (II). Polymerisation

of (I) with 1.0% H_2SO_4 in AcOH yields a *dimeride*, m.p. 66° , and *trimeric* $\beta\gamma$ -*dimethylbutadiene*. (I) with $\text{CHMe}:\text{CH}:\text{CO}_2\text{Et}$ affords *Et* 2 : 4 : 5-*trimethyl- Δ^4 -tetrahydrobenzoate*, b.p. $127\text{--}130^\circ/28$ mm., hydrolysed (KOH-EtOH) to the *acid*, m.p. 137° (*anilide*, m.p. 162°).

J. D. R.

Formation and structure of polymerides of the insoluble cross-linked type. R. G. W. NORRISH and E. F. BROOKMAN (Proc. Roy. Soc., 1937, A, 163, 205—220).—A series of cross-linking agents are described together with the properties of their copolymerides with monovinyl compounds. Support is given to Staudinger's view (the formation of three-dimensional macro-mols.) of the structure of these polymerides and a general formula is given. It is suggested that the electronic properties of the group X in the divinyl compound $(\text{CH}_2:\text{CH})_2\text{X}$ determines the cross-linking properties in the same way that the electronic properties of R in the monovinyl compound $\text{CH}_2:\text{CH}:\text{R}$ determines the ease of polymerisation of those compounds.

G. D. P.

Formation of benzene in the radiochemical polymerisation of acetylene. II. Quantity of benzene formed. C. ROSENBLUM (Bull. Soc. chim. Belg., 1937, 46, 503—518; cf. A., 1937, II, 236).—Polymerisation of C_2H_2 under the influence of α - and β -rays from Rn gives 20% conversion into C_6H_6 , the formation of which is attributed to the rearrangement of an active linear trimeride. The diminution of the C_6H_6 : cuprene ratio as the reaction proceeds is due to a secondary polymerisation of the C_6H_6 .

J. D. R.

Hydration of acetylenes. II. Δ^8 -Pentinine. Reactivity in homologous series. E. L. R. MOWAT and J. C. SMITH (J.C.S., 1938, 19—22).— Δ^8 -Pentinine with 80% H_2SO_4 at 0° yields about 50% each of COMePr^a and COEt_2 , the proportions of the ketones being determined by the m.p. of the mixture of semicarbazones and *p*-nitrophenylhydrazones. Together with the results of the hydration of Δ^0 -undecynoic acid (A., 1937, II, 440) this indicates that in the hydration of $\text{CMe}:\text{CR}$, the acetylenes display increasing reactivity with increasing length of alkyl chain due to the increase in negativity of C attached to alkyl.

J. D. R.

Interaction of alkyl iodides with sodium guaiacoxide in ethyl alcohol.—See A., I, 86.

Rate and mechanism of hydrolysis and alcoholysis of *tert*-butyl chloride. Application to the transition state theory of solvent effects.—See A., I, 86.

Classification of complexes of magnesium chloride with organic compounds containing oxygen according to nature of oxygen linking. M. L. QUINET (Compt. rend., 1937, 205, 675—677; cf. A., 1935, 179; 1937, I, 256).—The no. of org. mols. combining with 1 mol. of MgCl_2 depends on the nature of O linking in the org. mol., viz., 6 for OH-compounds (analogous to $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$), and 3 for CO-compounds. Ethers do not combine with MgCl_2 . Complexes of MgCl_2 with H_2O and alcohols do not react with aldehydes and ketones, whilst those with aldehydes and ketones are immediately decomposed by H_2O and

alcohols, thus providing a method of prep. of complexes of MgCl_2 with higher alcohols. Decomp. by heat gives in all cases MgO . Alcohols give immediately oxychlorides $\text{MgCl}_2\cdot 3\text{Mg}(\text{OR})_2$. Ketones give the 1 : 1 mol. compounds. Thus $\text{MgCl}_2\cdot 3\text{COMe}_2$ at 100° gives $\text{MgCl}_2\cdot \text{COME}_2$ and at 200° $\text{Mg}(\text{OEt})_2$, whilst at 56° dehydration occurs with formation of phorone and $\text{MgCl}_2\cdot 2\text{H}_2\text{O}$. E. G. B.

Decomposition of methyl alcohol over rhenium.—See A., I, 88.

Effect of alkali on copper methyl alcohol catalysts.—See A., I, 149.

Catalytic esterification of alcohols of the series $\text{C}_n\text{H}_{2n+1}\cdot\text{OH}$ without the participation of organic acids. M. M. KOTON (J. Gen. Chem. Russ., 1937, 7, 2188—2194).—The yields of esters obtained by passing EtOH, PrOH, or BuOH over Cu catalysts at 275° fall in the series Cu filings > Cu-Zr > pptd. Cu > Cu-Ce, whilst in the case of *iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$ the series pptd. Cu > Cu filings > Cu-Zr > Cu-Ce obtains. The yields of ester, acid, and aldehyde obtained with the above catalysts and alcohols are tabulated.

R. T.

Catalytic properties of cerium oxide.—See A., I, 88.

Spectrographic and chemical study of aliphatic terpenes. II. Alcohols and aliphatic aldehydes. G. DUPONT, V. DESREUX, and R. DULOU (Bull. Soc. chim., 1937, [v], 4, 2016—2026; cf. A., 1937, II, 200).—Raman spectral data indicate that geraniol (from Java citronella oil) does not contain α -geraniol, but that the terminal double linking observed is due to the presence of linalol. The Raman spectrum of pure β -geraniol has been determined. The product of catalytic hydrogenation over Ni (citronellol, not dehydrogeraniol) confirms the absence of α -geraniol in the original. The Raman spectra of geraniol and nerol are almost identical. The specimen of linalol examined consisted almost entirely of the β form; on catalytic hydrogenation (Ni or Pt) it yielded dihydrolinalol. Spectral data show that citral contains no α form, whilst citronellal is a mixture of β with α . On catalytic hydrogenation citral contains no α form, whilst citronellal is a mixture of β with α . On catalytic hydrogenation citral yields citronellal and then citronellol.

E. S. H.

Linolenyl alcohol. Preparation and properties. O. TURPEINEN (J. Amer. Chem. Soc., 1938, 60, 56—57).—Me linolenate and Na-BuOH give a 70—72% yield of *linolenyl alcohol*, m.p. -5° to -2° (*p*-nitrophenylurethane, m.p. $91\text{--}92^\circ$), which tends to "dry" in air and with PtO_2 in AcOH absorbs 2 H_2 to yield *n*- $\text{C}_{18}\text{H}_{37}\cdot\text{OH}$.

R. S. C.

Photochemistry of alkyl nitrites.—See A., I, 90.

Alkylation of reactive methylene groups with alkyl sulphates. E. BOWDEN (J. Amer. Chem. Soc., 1938, 60, 131).—Numerous compounds with reactive CH_2 are alkylated in satisfactory yield by Et_2SO_4 and NaOEt or NaNH_2 . Examples are $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$, camphor, $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$, BuCN, COPhMe, COMeBu, etc.

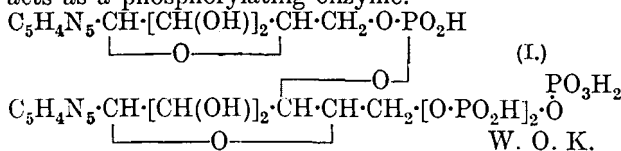
R. S. C.

Steric correspondence of the biological glycerol- α -phosphoric acid and β -phosphoglyceric acid. W. KIESSLING and P. SCHUSTER (Ber., 1938, 71, [B], 123—128).—The biological (—)-glyceryl- α -phosphoric acid (I) (as Ba salt) is oxidised by Br in alkaline solution to (+)- β -phosphoglyceric acid (II), $[\alpha]_D^{20} +13.6^\circ$. The compound cannot be fermented and is not esterified with glucose through phosphopyruvic acid to AcCO_2H and hexose monophosphate. Its Ba H salt is identical with that of the natural acid. Independent evidence of the steric correspondence of (I) and (II) is furnished by the hydrolysis by N-HCl at 126° of (II) to Ba glycerate, $[\alpha]_D^{20} -10^\circ$, whilst for the hydrolysate of the biological (—)- β -phosphoglyceric acid the val. $[\alpha]_D^{20} +12^\circ$ is determined. H. W.

Synthesis of phosphatides. I. Synthesis of dipalmityl- β -kephalin and dipalmityl- β -lecithin. I. KABASHIMA (Ber., 1938, 71, [B], 76–80).— β -Glycerolphosphoric acid is separated from technical Na glycerophosphate as the compound of its Ba salt with $\text{Ba}(\text{NO}_3)_2$ and converted by palmityl chloride into $\alpha\alpha'$ -dipalmitylglyceryl- β -phosphoric acid, the Ag salt (I) of which is transformed by β -bromoethylamine picrate in $\text{CHCl}_3\text{-COMe}_2$ at 85–90° into dipalmityl- β -kephalin. *Dipalmityl- β -lecithin*, m.p. 181°, is obtained analogously from (I) and *trimethyl- β -bromoethylammonium picrate*, m.p. 158–159°. NMe_3 and $\text{C}_2\text{H}_4\text{Br}_2$ at 125–130° give *trimethyl- β -bromoethylammonium bromide*, m.p. 223° (decomp.).

H. W.

Dinucleotidepyrophosphoric acid of yeast. W. KIESSLING and O. MEYERHOF (Naturwiss., 1938, 26, 13—14).—The $\text{CCl}_3\cdot\text{CO}_2\text{H}$ extract of fresh beer yeast contains a substance which on esterification with phosphopyruvic acid in presence of rabbit-muscle extract yields the pyrophosphoric acid derivative of diadenosine-5' : 5'-diphosphoric acid, to which on the basis of its composition and properties formula (I) is assigned. (I), $[\alpha]_{\text{D}}^{20} -39.2^\circ$ in $\text{N-H}_2\text{SO}_4$ (calc. on the basis of adenylic acid content), yields a *Ag* salt, $\text{C}_{20}\text{H}_{24}\text{O}_{19}\text{N}_{10}\text{P}_4\text{Ag}_4$, and on alkaline hydrolysis yields adenosinepyrophosphoric acid (1 mol.) and adenylic acid (1 mol.). Apparently the greater part of the adenosine-5'-phosphoric acid, of yeast exists as the dinucleotide which, like adenylic acid, acts as a phosphorylating enzyme.



W. O. K.

Preparation of esters. III. F. ADICKES [and, in part, M. MEISENHEIMER and G. HINDERER] (J. pr. Chem., 1938, [ii], 150, 81—94; cf. A., 1936, 1251).— α -*Dichloroisobutryl chloride*, b.p. 156—162°/740 mm., from $\text{Pr}^\beta\text{COCl}$ and Cl_2 at 40—50°, gives with EtOH *Et* α -*dichloroisobutyrate*, b.p. 188—189°/735 mm. $\text{COBu}^\gamma\text{CHNa}\cdot\text{CO}_2\text{Et}$ and EtI give *Et* β -*keto- γ -methyl- α -ethylisovalerate*, b.p. 109°/16 mm., converted by Br in boiling CCl_4 into the α -*Br-ester*, b.p. 131°/16 mm. $\text{CHMe}(\text{CO}_2\text{Et})_2$ and S_2Cl_2 give *Et*₂ α -*chloro(methylmalonate)*, b.p. 102—103°/12 mm. Irradiating $\text{CH}_3\text{Ph}\cdot\text{COCl}$ and Br and pouring the product into

EtOH gives 5% of *Et* α -dibromo- α -phenylacetate, b.p. 170°/15 mm. *Me* 2 : 2'-diphenylenebenzylpyruvate, m.p. 117—119°, is obtained with 9-benzylfluorene from $(C_6H_5)_2C:C(ONa) \cdot CO_2Me$ and CH_2PhCl in hot Et_2O . *p*- $C_6H_4Me \cdot SO_2Na$ and the appropriate Cl-ester in EtOH give *Et* *p*-toluenesulphonyl-phenyl-, m.p. 113.5—114°, and -diphenyl-acetate, m.p. 126—127°, *Et_2* *p*-toluenesulphonylmalonate, m.p. 39—40°, and *Et* α -*p*-toluenesulphonylisobutyrate, m.p. 79—80°. $CHPh(CO_2Me)_2$ with S_2Cl_2 or Cl_2 gives *Me_2* α -chloro(phenylmalonate), m.p. 57—57.5°. The prep. of *Et* 2 : 4 : 6-trinitrobenzoate, phenylcyanoacetate, mandelate, benzilate, α -chlorodiphenylacetate, Et_2 , forms, m.p. 74—76° and 89—90°, and *Me_2* 2 : 2'-diphenylene-pyruvate, forms, m.p. 127—128° and 117.5°, is improved. $MeCHO$ and *p*- $C_6H_4Me \cdot SH$ in $AcOH$ give acetaldehyde di-*p*-tolyl mercaptal, oxidised by $KMnO_4$ to ethylidene *p*-tolyl sulphoxide *p*-tolyl sulphone, m.p. 112—113°, and a substance (? the disulphone), m.p. 108—109°. 9-Fluorenyl *p*-tolyl sulphone does not react with CH_3N_3 . R. S. C.

Action of ammonia on esters. H. E. FRENCH and G. G. WRIGHTSMAN (J. Amer. Chem. Soc., 1938, 60, 50—51).—The rate of reaction of 13 simple alkyl acetates with aq. NH_3 is reported. The rate decreases with increase in mol. wt. and with introduction of side-chains, the more so the closer is the side-chain to the O. *tert*.-Alkyl esters react more slowly than *sec*.-alkyl esters. Hydrolysis always occurs as well as formation of the amide and is depressed by similar influences, but to a smaller extent. R. S. C.

Isotopic exchange reactions of organic compounds. II. Survey of the monocarboxylic acid series. III. Kinetics of the isomerisation and isotope exchange of vinylacetic acid. D. J. G. Ives (J.C.S., 1938, 81—91, 91—97).—The partition of D and H between monocarboxylic acids and dil. D₂O at 100° in presence of 1.05 mol. of NaOH is studied by the method described previously (A., 1935, 1350) modified and improved for the determination of *d*, to an accuracy of a few p.p.m., with small samples. With AcOH, exchange of C-H for C-D occurs in alkaline but not in neutral solution. Phenylacetic, acrylic, crotonic, and sorbic acids undergo alkali-catalysed exchange reactions, but propionic, isobutyric, benzoic, *p*-toluic, α - and β -phenylpropionic, and cinnamic acids do not. No exchange accompanies the acid hydrolysis or saponification of EtOAc. These results are discussed in relation to the mechanism of exchange reactions with reference to evidence available from chemical reactions and to theories of structure.

III. It is shown that the exchange reaction of vinylacetic acid proceeds faster than the isomerisation to crotonic acid, the respective velocity coeffs. being 0.009 and 0.0038 min.⁻¹, indicating that the isomerisation is a bimol. reaction. A kinetic proof is given that the D:H ratio in the α -position of the β -isomeride in equilibrium with the solvent is unchanged during the formation of the intermediate ions postulated by the prototropic theory of three-C tautomerism. On the basis of the constancy of the D:H ratio in the α -position, the relative rates of removal from, and addition to, the vinylacetic acid

mols. of protons and deuterons are found to be 3.15 and 3.55, giving a val. of 0.89 for the exchange equilibrium const.

J. D. R.

Action of concentrated sulphuric acid on oleic acid. A. STEGER, J. VAN LOON, (FRL.) B. R. N. VELLENGA, and B. PENNEKAMP (Rec. trav. chim., 1938, 57, 25—32).—Oleic acid when treated with conc. H_2SO_4 and the resulting sulphuric ester hydrolysed with H_2O yields a mixture of hydroxystearic acids, which on distillation gives a mixture of solid (66%) and liquid acids (34%). The solid acids with O_3 in CHCl_3 yield sebacic, azelaic, and suberic acids, and must be a mixture of Δ^7 -, Δ^8 -, and Δ^9 -elaidic acids. Similarly, the liquid acids are shown to be a mixture of Δ^7 -, Δ^8 -, and Δ^9 -oleic acids. Ozonisation of a technical product rich in "isooleic acid" also shows the presence of the three isomeric elaidic acids above.

E. I.

Fatty acids. III. Properties of linoleic acids prepared by debromination and by low-temperature crystallisation. Quantitative determination. J. B. BROWN and J. FRANKEL (J. Amer. Chem. Soc., 1938, 60, 54—56; cf. A., 1937, II, 84).—380 g. of 93.5% pure α -linoleic acid (I) are obtained by crystallisation from 2 kg. of the unsaturated acids of maize oil. The acid is identified with that prepared by debromination. Under standard conditions (I) gives 0.906 times its wt. of solid tetrabromide (theory 2.14), a proportion which can be used for determining (I).

R. S. C.

Action of oxalic acid on a cobaltic chloropentammine.—See A., I, 156.

Additive compound of oxalyl chloride and dioxan. G. A. VARVOGLIS (Ber., 1938, 71, [B], 32—34).—Addition of $(\text{COCl})_2$ in light petroleum to dioxan (I) in the same solvent at -5° to -7° gives the additive compound, $\text{C}_4\text{H}_8\text{O}_2 \cdot \text{C}_2\text{O}_2\text{Cl}_2$, m.p. $67-68^\circ$ (slight decomp.), which can be kept for months in a sealed tube in absence of air, but loses (I) when exposed to air, after which the $(\text{COCl})_2$ is hydrolysed by atm. moisture. In freezing C_6H_6 the compound appears extensively solvolyzed. $(\text{COCl})_2$ does not give analogous compounds with Et_2O or diisomyl ether and (I) does not appear to react with AcCl , BzCl , $\text{CH}_2(\text{COCl})_2$, fumaryl, succinyl, *s*- or *as*-phthalyl, or terephthalyl chloride.

H. W.

Addition of malonic enolates to $\alpha\beta$ -unsaturated ketones. A. MICHAEL (J. Org. Chem., 1937, 2, 303—307; cf. A., 1931, 67, 603; 1932, 252; 1933, 608).—The anomalous $\alpha\delta$ -addition of malonic enolates to $\alpha\beta$ -acetylenic esters found by Kon *et al.* (A., 1932, 601, 1127; 1937, II, 48) is discussed in relation to energy and chemical affinity. The reaction course is governed by the max. possible neutralisation of Na in the resulting enolates. Thus Na in the $\alpha\delta$ -additive products

$(\text{CO}_2\text{Et})_2\text{CR} \cdot \text{CR}'\text{:C}(\text{ONa})\text{OEt}$ (I) is better neutralised than in the corresponding $\alpha\beta$ -products $\text{CO}_2\text{Et} \cdot \text{CHR} \cdot \text{CHR}'\text{:C}(\text{CO}_2\text{Et})\text{:C}(\text{ONa})\text{OEt}$ from $\alpha\beta$ -ethylenic esters. The anomalous γ -alkylation of (I) with $\text{R} = \text{H}$ with EtI whilst (I) with $\text{R} = \text{Me}$ gives $(\text{CO}_2\text{Et})_2\text{CMe} \cdot \text{CR}'\text{:C}(\text{Et})\text{CO}_2\text{Et}$ is due to the γ -Me of (I) with $\text{R} = \text{Me}$ being more strongly attached than

the γ -H when $\text{R} = \text{H}$. The contention of Kon *et al.* (*loc. cit.*) and of Holden and Lapworth (A., 1931, 1271) that in $\text{CHMe}(\text{CO}_2\text{Et})_2$ (II) additions to $\alpha\beta$ -unsaturated esters, the $\alpha\beta$ -Me₂ ester (III) is in all cases formed by rearrangement of the $\beta\gamma$ -Me₂ ester (IV) first formed and that unless NaOEt is present the latter is formed, is refuted. Thus (II) with $\text{CHR} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$ (V) in presence of NaOEt gives $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CHR} \cdot \text{CMe}(\text{CO}_2\text{Et})_2$ (VI), whilst $\text{CO}_2\text{Et} \cdot \text{CMe} \cdot \text{C}(\text{ONa}) \cdot \text{OEt}$ with (V) gives $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{CHR} \cdot \text{C}(\text{CO}_2\text{Et})\text{:C}(\text{ONa})\text{OEt}$ and not the Na enolate of (VI). An explanation of the alleged formation of (III) from (IV) based on formation of an intermediate C_4 -ring by elimination of EtOH, followed by fission and addition of EtOH, is untenable since such rings are stable to EtOH. Additive reactions of enolates cannot therefore be explained on the basis of valency alone. E. G. B.

Single- and double-shelled malonato-complexes and double-shelled succinato-complexes.—See A., I, 92.

Maleic acid production. Vapour-phase oxidation of crotonaldehyde using vanadium pentoxide catalysts. W. L. FAITH and A. M. SCHAIBLE (J. Amer. Chem. Soc., 1938, 69, 52—54).—Increasing the ratio of air to $\text{CHMe} \cdot \text{CH} \cdot \text{CHO}$ increases the amount of maleic anhydride formed in presence of V_2O_5 at $250-600^\circ$. V_2O_5 on Al gives higher yields than does V_2O_5 on pumice owing to the greater thermal conductivity of the former. For V_2O_5 on pumice the optimum temp. is 350° (31.8% yield with a 325 : 1 air-aldehyde mixture); for V_2O_5 on Al it is 450° (44.5% yield with a 520 : 1 mixture). R. S. C.

Non-reaction of acetylketen and maleic anhydride and some notes on maleic acid. C. D. HURD, A. S. ROE, and J. W. WILLIAMS (J. Org. Chem., 1937, 2, 314—318; cf. A., 1936, 967).— $\text{CHAc} \cdot \text{CO}$ does not react with furan or with maleic anhydride (I), but with (I) a slight separation of maleic acid (II) occurs, also observed with (I) and $\text{CH}_2\text{Ac} \cdot \text{CO}_2\text{Et}$. The acid has m.p. 137° (lit. m.p. $130-131^\circ$) (cf. A., 1907, i, 1063; 1908, i, 735). Its nature is shown by its mixed m.p. with the product, m.p. 136° , obtained from (I) and H_2O , and by the prep. in full yield from all specimens by action of Ac_2O and the appropriate amine of *N*-*p*-tolylmaleamic acid, new m.p. 195° , and *N*-4-methoxyphenylmaleamic acid, new m.p. 186° . All specimens of (II) on remelting have m.p. $130-131^\circ$, due to partial isomerisation to mixtures containing 3% of fumaric acid (III). Repeated fusions of (II) do not give a m.p. $<130^\circ$ owing to the slight solubility of (III) in the fused mixtures.

E. G. B.

Double-shelled citrato-complexes of various cobaltic and chromic amines in the dissolved state.—See A., I, 92.

Calcium borogluconate. H. T. MACPHERSON and J. STEWART (Biochem. J., 1938, 32, 76—78).—Ca borogluconate is formed from 1 mol. of Ca gluconate and 2 mols. of H_3BO_3 by loss of H_2O . In H_2O , it behaves as a mixture of these substances. The product of Dryerre and Greig (A., 1935, 775) is a mixture of Ca mono- and di-borogluconates. J. N. A.

Stability of the free formyl radical. M. BURTON (J. Amer. Chem. Soc., 1938, 60, 212).—Published evidence supports the existence and stability of HCO. R. S. C.

Formylation of carbon atoms by the method of amide condensation. G. V. TSCHELINGEV and B. M. DUBININ (J. Gen. Chem. Russ., 1937, 7, 2309—2313).—HCO·NPh₂, NaOEt, and COMe₂, COPhMe, or camphor yield respectively CH₂Ac·CHO, CH₂Bz·CHO, or formylcamphor. R. T.

Depolymerisation process in formaldehyde solutions.—See A., I, 147.

Chemistry of chloral and chloral hydrate. N. W. HIRWE (J. Univ. Bombay, 1937, 6, Part II, 182—198).—A review.

Synthesis of Δ^8 -octadienal. G. GOETHALS (Bull. Acad. roy. Belg., 1937, [v], 23, 721—738).—Me Δ^8 -pentenoate is reduced with MeOH and Na at 60° to a 3:1 mixture, b.p. 53—54°/20 mm., of Δ^7 -pentenol [chloride (I), b.p. 107—107·6°/755 mm.; iodide (II), b.p. 53·6°/20 mm.], *n*-pentanol, and smaller amounts of methoxyamyl alcohol and β - or γ -methoxyvaleric acid. The Grignard reagent from a mixture of (I) and (II) when treated with acetaldehyde affords Δ^8 -octadienol, b.p. 72·5—75·5°/10 mm., converted by PBr₃ and C₅H₅N into a mixture of primary and sec.-bromides, b.p. 72—83°/10 mm. The latter is treated with AgOBz, the benzoates are separated by fractional distillation, and the purity is checked by the Raman spectra. On hydrolysis with KOH-MeOH, the purified ester gives Δ^8 -octadienol, b.p. 88—90·5°/10 mm., containing about 12% of octenol, which with K₂Cr₂O₇-H₂SO₄ affords trans- Δ^8 -octadienal, b.p. 77—79°/10 mm. (semicarbazone, m.p. 169·3—170°). The aldehyde resinifies on keeping and has a somewhat irritating, much less pleasant odour than the nonadienal. The optical properties of the above compounds, including the Raman spectra, are discussed. S. C.

Two alkoxyacetaldehydes. Their preparation and properties. N. L. DRAKE, H. M. DUVAL, T. L. JACOBS, H. T. THOMPSON, and H. M. SONNICHSEN (J. Amer. Chem. Soc., 1938, 60, 73—76).—Passage of OMe·[CH₂]₂·OH over Cu at 425° gives the max. yield of OMe·CH₂·CHO, b.p. 92°/770 mm., which yields a *p*-nitro-, m.p. 115—115·5°, and 2:4-dinitro-phenylhydrazone, m.p. 124—125°, and an azeotropic mixture, b.p. 88·5°/770 mm., with 12·8% of H₂O; no semicarbazone could be isolated. OEt·[CH₂]₂·OH and Cu at 300° give 43% of ethoxyacetaldehyde, b.p. 105—106° (*p*-nitro-, m.p. 113—114°, and 2:4-dinitro-phenylhydrazone, m.p. 116—117°), which gives an azeotropic mixture, b.p. 90—91°, with 21·8% of H₂O. Both aldehydes polymerise to liquid trimers, depolymerised by distillation with a trace of *p*-C₆H₄Me·SO₃H in very poor and 40—50% yield, respectively. The OMe-aldehyde gives also a tetrameride, m.p. 142—142·5°. OBu·[CH₂]₂·OH gives less readily butoxyacetaldehyde, b.p. 130—135°. R. S. C.

Preparation of ketones from higher fatty acids. V, VI. K. KINO (J. Soc. Chem. Ind. Japan, 1937, 40, 437—438B; cf. A., 1937, II, 483).—V. The D** (A., II.)

frothing of 40 g. of fatty acid (usually stearic) with 1·8 g. of Mg at 330—340° is completely prevented by 5—10 g. of Cr soap and diminished by 10 g. of Ca soap. 10 g. of Ba soap stops both frothing and formation of ketone. Zn, Ni, Mg, Cu, Al, and Pb soaps are without effect.

VI. Mn, Zn, and Mg soaps decompose slowly at 250—260°, 300—310°, and 280—290°, and rapidly at >300°, >330—340°, and 330—340°, respectively. R. S. C.

Amine catalysis of the dealdolisation of diacetone alcohol. F. H. WESTHEIMER and H. COHEN (J. Amer. Chem. Soc., 1938, 60, 90—94).—The rate of dissociation of OH·CMe₂·CH₂·COMe (I) in NH₂Me-NH₃MeCl, NHMe₂-NH₂Me₂Cl, NMe₃-NHMe₃Cl, and NEt₃-NH₂Et₃Cl to COMe₂ at 18° is pseudo-unimol., being independent of the concn. of (I). With NH₂Me or NHMe₂ it is dependent on the [OH⁻] and on the concn. of mol. amine, but with NMe₃ or NEt₃ is independent of the latter. The reaction is thus not one of general base catalysis, and the slow step is probably O⁻·CMe₂·CH₂·COMe → COMe₂ + COMe·CH₂⁻. With NH₂Me and NHMe₂, however, some intermediate, possibly a ketimine, involving the H attached to N, must be formed. R. S. C.

Absorption spectra of carbohydrates in sulphuric acid.—See A., I, 59.

Active form of monosaccharides. III.

Mechanism of addition of hydrocyanic acid.

IV. **Reactivity of glucose-6-phosphate.** A. V.

STEPANOV and B. N. STEPANENKO (Biochimia, 1937, 2, 875—893, 917—925).—III. The catalytic effect of addition of bases to solutions of sugars (glucose, galactose, fructose) and HCN is at a max. when the entire HCN is neutralised. The reaction of cyanohydrin formation is represented: >C:O + NH₄⁺ ⇌

$\begin{matrix} \text{ON}^+ \\ \text{:C:ONH}_4 \end{matrix} \rightleftharpoons \begin{matrix} \text{H}_2\text{O} \\ \text{:C(ONH}_4\text{):CN} \end{matrix} \longrightarrow \begin{matrix} \text{H}_2\text{O} \\ \text{:C(OH):CN} \end{matrix} + \text{NH}_3$
+ H₂O. The reaction proceeds in 10% but not in 80% MeOH, in which ionisation of NH₄CN is suppressed. The velocity of reaction in presence of C₅H₅N or piperidine ∝ dissociation consts. of the cyanides formed, but is smaller with NMe₃ than with NH₃, showing that not only the dissociation const. of the salt, but also the nature of the cation, influences the reaction.

IV. **Cyanohydrin formation is more rapid with Ba glucose-6-phosphate than with glucose, in presence or absence of NH₃.** R. T.

Reaction of monosaccharides with phenylhydrazine in presence of sodium hydrogen sulphite. A. D. BRAUN (Biochimia, 1937, 2, 801—807).—Fructose in aq. NaHSO₃ yields a cryst. phenylhydrazide with NPh·NH₂ at 10°; under these conditions aldoses (glucose, mannose, galactose, arabinose) do not react. Production of fructose by heating glucose with dil. AcOH is confirmed. R. T.

Syntheses with 5:6-anhydroisopropylidene-glucose. V. **6-Diphenylamino-*d*-chinovose [6-*d*-glucosyldiphenylamine].** H. OHLE and M. ANDRÉE (Ber., 1938, 71, [B], 27—31; cf. A., 1936, 1491).—Anhydroisopropylideneglucose and NPh₂ at 135—137° give 6-diphenylaminoisopropylidene-chinofuranose (I), m.p. 124°, [α]_D²⁰ -73·3° in CHCl₃,

—46.7° in AcOH, better obtained at 100° in the absence of air. It gives a *diacetate*, m.p. 124°, $[\alpha]_D^{20}$ —6.1° in CHCl_3 , which dissolves slowly and without yielding a cryst. product in Br-AcOH, and a 3 : 5-*di-p-toluenesulphonate*, m.p. 145°, $[\alpha]_D^{20}$ —49.1° in CHCl_3 . Hydrolysis of (I) in PrOH in absence of air gives 6-*diphenylamino-β-d-chinowose*, which separates from MeOH as the *monohydrate* (II), m.p. 90—91°, decomp. >100°, $[\alpha]_D^{20}$ —37.2° (no mutarotation) in COMe_2 . Slight and slow mutarotation is observed in $\text{C}_5\text{H}_5\text{N}$ or MeOH with or without NaOH. In 5*N*-HCl the sugar has $[\alpha]_D^{20}$ +111.2°. The absence of mutarotation is not due to the rapidity with which equilibrium is established but to the great stability of the β-variety. Treatment of (II) with Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 0° gives 6-*diphenylamino-β-d-chinopyranose tetraacetate* (III), m.p. 190—191°, $[\alpha]_D^{20}$ +7.18° in CHCl_3 , $[\alpha]_D^{25}$ —5.0° in COMe_2 , readily transformed by HBr-AcOH into 6-*diphenylamino-α-d-chinopyranosyl 1-bromide triacetate* (IV), m.p. 147—148°, $[\alpha]_D^{20}$ +102.2° in CHCl_3 , re-converted by AgOAc in AcOH into (III). (IV) and Ag_2CO_3 in MeOH at 20° yield 6-*diphenylamino-β-methyl-d-chinopyranoside 2 : 3 : 4-triacetate*, m.p. 128—129°, $[\alpha]_D^{21}$ —53.1° in MeOH, $[\alpha]_D^{20}$ —46.4° in COMe_2 , —55.9° in CHCl_3 , hydrolysed by NaOMe in MeOH to 6-*diphenylamino-β-methyl-d-chinopyranoside*, m.p. 208°, $[\alpha]_D^{25}$ —29.0° in COMe_2 . H. W.

Reaction for distinguishing fructose from glucose. E. V. ZMAČINSKI (Compt. rend. Acad. Sci. U.R.S.S., 1937, 17, 415—416).—When warmed with a small quantity of S, glycerol, and aq. $\text{Pb}(\text{OAc})_2$, fructose, but not glucose, gives a black colour.

J. D. R.

Acetals of galactose and of dibenzylidene-glucose. M. L. WOLFROM, L. J. TANGHE, R. W. GEORGE, and S. W. WAISBROT (J. Amer. Chem. Soc., 1938, 60, 132—134).—Dibenzylideneglucose Et_2 mercaptal 6-benzoate, CdCO_3 , and HgCl_2 in EtOH at 70—80° give *dibenzylidene-d-glucose Et₂ acetal 6-benzoate* (I), m.p. 141—143°, $[\alpha]_D^{28}$ +14° in CHCl_3 . Dibenzylideneglucose Et_2 mercaptal gives similarly *dibenzylidene-d-glucose Et₂ acetal*, m.p. 133—135°, $[\alpha]_D^{28}$ +16° in CHCl_3 , also obtained from (I) by hot 0.5*N*-NaOEt and converted into (I) by $\text{BzCl}-\text{C}_5\text{H}_5\text{N}$. The Me_2 acetal 6-benzoate, m.p. 156—159° after softening at 142°, $[\alpha]_D^{24}$ +14° in CHCl_3 , is similarly prepared, and the appropriate galactose mercaptals afford *d-galactose Et₂*, m.p. 79°, $[\alpha]_D^{20}$ +17.5° in CHCl_3 , and Me_2 acetal *penta-acetate*, m.p. 128—129°, $[\alpha]_D^{20}$ +16° in CHCl_3 , hydrolysed by 0.7*M*-Ba(OMe)₂ at 0° to *d-galactose Et₂*, m.p. 127—128°, $[\alpha]_D^{20}$ +15° in H_2O , and Me_2 acetal, m.p. 122—123°, $[\alpha]_D^{28}$ +16° in H_2O . R. S. C.

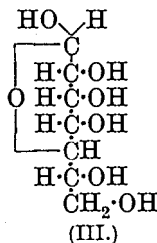
l-Talose. C. GLATTHAAR and T. REICHSTEIN (Helv. Chem. Acta, 1938, 21, 3—6).—*l*-Galactonolactone is transformed by H_2O and $\text{C}_5\text{H}_5\text{N}$ at 135° into *l*-talonic acid, conveniently isolated as the *K* salt, m.p. 170—171° (corr.), $[\alpha]_D^{24}$ —1.2° in H_2O . This is transformed by dil. H_2SO_4 into *l-talonolactone*, m.p. 134—136° (corr.), $[\alpha]_D^{25}$ +32.4° in H_2O , which is reduced by Na-Hg in slightly acid solution to non-cryst. *l-talose* (I), $[\alpha]_D^{24}$ —16.9° in H_2O (*o*-nitro-

phenylhydrazone, m.p. 144—146°, $[\alpha]_D^{26}$ —77.4° in MeOH). H. W.

Complete acetylation and methylation of α-*d*-tagatose. Y. KHOUVINE and Y. TOMODA (Compt. rend., 1937, 205, 1414—1415).—Treatment of α-*d*-tagatose with Ac_2O and ZnCl_2 at 0° or 50° does not give a cryst. product, whereas with Ac_2O and $\text{C}_5\text{H}_5\text{N}$ at —5°, 0°, or 20—30°, α-*d*-tagatopyranose *penta-acetate*, m.p. (block) 132°, $[\alpha]_D^{20}$ +20° in CHCl_3 , —25° in MeOH, results. It does not add H in presence of Raney Ni and its ultra-violet spectrum has not the characteristic ketonic band. Tagatose tetra-acetate could not be obtained cryst. Methylation of α-*d*-methyltagatoside by NaOH and Me_2SO_4 gives only incompletely methylated syrups, whereas very frequently repeated treatments with MeI and Ag_2O leads to α-*pentamethyltagatopyranoside* (I), b.p. 40°/10^{−4} mm., $[\alpha]_D^{20}$ +21.4° in MeOH. The cyclic structure is established by the Raman spectrum and refractive index. Hydrolysis of (I) with 0.72% HCl at 100° gives *tetramethyltagatose*, b.p. 52°/10^{−4} mm., $[\alpha]_D^{27.8}$ —3.4° in MeOH. H. W.

Guloheptonic acids; α-*d*-α-guloheptose. H. S. ISBELL (J. Res. Nat. Bur. Stand., 1937, 19, 639—650).—Treatment of the compound, *d*-gulose, $\text{CaCl}_2 \cdot \text{H}_2\text{O}$, with NaCN followed by $\text{Ca}(\text{OH})_2$ gives ppts. of the basic Ca salts of the epimeric guloheptonic acids. Decomp. of the mixture with aq. H_2SO_4 and concn. of the resulting solution affords *d-α-guloheptonic acid* (I), $\text{C}_7\text{H}_{14}\text{O}_8$, m.p. 128°, $[\alpha]_D^{20}$ —12.6°. *d-α-Guloheptono-γ-lactone* (II), $\text{C}_7\text{H}_{12}\text{O}_7$, m.p. 145°, $[\alpha]_D^{20}$ +25.5°, and the *phenylhydrazide*, m.p. 156°, $[\alpha]_D^{20}$ +29.3°, *Pb*, $[\alpha]_D^{20}$ —6.6°, and *Ba*, $[\alpha]_D^{20}$ —1.4°, salts of (I) are described. The mother-liquors from (I) yield *d-β-guloheptonic acid*, m.p. 135°, $[\alpha]_D^{20}$ +12.8° (*Pb*, $[\alpha]_D^{20}$ +16.7°, and *Ba*, $[\alpha]_D^{20}$ +1.5°, salts). Reduction of (II) with Na-Hg yields α-*d*-α-guloheptose (III), $\text{C}_7\text{H}_{14}\text{O}_7$, m.p. 127°, $[\alpha]_D^{20}$ —45.7° to —16.9° (equilibrium) in H_2O . Observations of mutarotation at 20.1° and 0.3° show a fast change accompanied by a smaller slow change; hence the equilibrium solution contains at least three modifications of the sugar in dynamic equilibrium. The proportions of the constituents involved in the rapid reaction vary with the temp. so that a change in temp. results in rapid mutarotation. The temp. coeff. for the rapid mutarotation reaction corresponds with those for the rapid reactions which cause the deviations in the mutarotations of galactose (IV), arabinose, talose, ribose, and *d*-β-guloheptose, whereas the temp. coeffs. for the slow change agree with those for the slow reactions which cause the normal mutarotations of glucose, mannose, (IV), gulose, and talose. The structure, reactions, and properties of (III) resemble those of α-*d*-talose and provide additional evidence that the properties of the sugars are determined in large measure by the configuration of five C atoms comprising the pyranose ring. H. W.

A holodiglucoside obtained from sophora-flavonolioside. J. RABATÉ and J. DUSSY (Compt. rend., 1937, 205, 1431—1433; cf. A., 1936, 768).—



Hydrolysis of sophoraflavonolside with boiling 0.2% H_2SO_4 gives campherol and *sophorose*, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, m.p. (block) 195–196°, $[\alpha]_D^{25} +37^\circ$ to $+22^\circ$. It contains 8 OH and one free $\cdot\text{CHO}$. It is hydrolysed by boiling 1.5% H_2SO_4 or by emulsin to glucose. It is not identical with gentiobiose or cellobiose.

H. W.

Configurative relationship of γ -heptylamine to norleucine. P. A. LEVENE and M. KUNA (J. Biol. Chem., 1938, 122, 291–295).—(+)- γ -Heptylamine is structurally correlated with (+)- β -hexylamine. (–)- γ -Amino- Δ^a -heptene (A., 1937, II, 437) with Ac_2O – $\text{C}_5\text{H}_5\text{N}$ yields (–)-*acet- Δ^a - γ -heptenylamide*, b.p. 105–110°/1.5 mm., $[\alpha]_D^{25} -0.75^\circ$, ozonised to (+)- *α -acet-amidoheptaldehyde*, b.p. 130–135°/3 mm., $[\alpha]_D^{25} +5.7^\circ$ in Et_2O , which is reduced (Adams) to (+)- *β -acet-amidoheptyl alcohol (acetylnorleucinol)*, b.p. 150–165° (bath)/0.1 mm. (micro-distilling flask described), $[\alpha]_D^{25} +3.6^\circ$ in EtOH , also obtained, b.p. 135–150° (bath)/0.1 mm., $[\alpha]_D^{25} +2.1^\circ$ in EtOH , from (–)-norleucinol (A., 1937, II, 139), already structurally correlated with (+)- β -hexylamine and with (–)- α -aminohexoic acid.

E. W. W.

Ammines of the Roussin's black salt series.—See A., I, 94.

Formation and decomposition of amino-acids by intermolecular transference of amino-groups. II. Equilibrium reaction between *l*(+)-glutamic and pyruvic acids, and between *l*(+)-alanine and α -ketoglutaric acid. A. E. BRAUNSCHEIN and M. G. KRITZMAN (Biochimia, 1937, 2, 859–874).—Equilibrium is attained in the reaction glutamic acid + pyruvic acid \rightleftharpoons alanine + α -ketoglutaric acid in 20–25 min. at 37°, in presence of muscle pulp, with addition of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na}$ and Na_2HAsO_3 to inhibit glycolysis and oxido-reduction reactions. The equilibrium mixture contains approx. equal amounts of the substrates.

R. T.

Simple synthesis of *dl*-citrulline. A. C. KURTZ (J. Biol. Chem., 1938, 122, 477–484).— α -Carbamido-arginine (A., 1936, 59) is converted by $\text{Ba}(\text{OH})_2$ and H_2SO_4 into *dl*-ornithine monosulphate. This when boiled in H_2O with CuO yields *dl*-ornithinecopper sulphate, which with $\text{CO}(\text{NH}_2)_2$ yields the Cu derivative of *dl*-citrulline (I) [m.p. 220–221° (decomp.) confirmed; cf. A., 1932, 196], which is liberated by H_2S . It is suggested that (I) has the structure

$[\text{NH}_2\cdot[\text{CH}_2]_3\cdot\text{CH} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{CO}\cdot\text{O} \end{smallmatrix}]_2\text{Cu}$, and that the $\alpha\text{-NH}_2$ is thus protected by the co-ordinate linking. The CuCl_2 derivative of *dl*-lysine similarly gives a product which is apparently ϵ -carbamidolysine. E. W. W.

Synthesis of *r*- α -amino- β -hydroxy-*n*-butyric acid. E. ABDERHALDEN and W. STENGER (Z. physiol. Chem., 1938, 251, 171–182).—Repetition of the work of Abderhalden and Heyns (A., 1934, 638) except in that the hydrolysis of Me α -bromo- β -methoxybutyrate is interrupted as soon as dissolution of the ester is complete gives an acid which becomes partly cryst., m.p. 59°. Amination of the separated portions gives the same α -amino- β -hydroxybutyric acid (I), decomp. 237–239°; this product from either

source gives the same Bz_1 , m.p. 176°, and Bz_2 , m.p. 174°, derivatives and the same α -benzenesulphonamido- β -hydroxybutyric acid, m.p. 162°. Reduction of the two acids by P and HI (*d* 2.0) at 150° gives the same α -aminobutyric acid; α -benzenesulphonamidobutyric acid has m.p. 145°, whereas the corresponding β -compound melts at 120°. Coupling of (I) with *dl*- α -bromoisohexoyl chloride affords two *dl*- α -bromoisohexoamido-*dl*- β -hydroxybutyric acids, (II), m.p. 155°, and (III), m.p. 122°; the latter is attacked by trypsin whereas the former is not. Amination of (III) leads to α -*dl*-leucylamino- β -hydroxybutyric acid, decomp. 193°, which is hydrolysed by erepsin; the isomeric compound, decomp. 233°, remains unattacked. Hydrolysis of (III) yields an *r*- α -amino- β -hydroxybutyric acid (IV), decomp. 227–229° after darkening at 215°, whereas (II) gives an isomeric acid (V), decomp. 239–241° after darkening at 225°; the mixed m.p. is about 231° after becoming brown at 215°. The Bz_1 and Bz_2 derivatives of (IV) have m.p. 178° and 147–148°, respectively, whilst the corresponding derivatives of (V) melt at 176° and 174°, respectively. (V) appears identical with the *dl*-allo-threonine of West and Carter (A., 1937, 328) but (IV) cannot be immediately identified with threonine. Injection of (IV) into the rabbit causes appearance in the urine of a dextrorotatory compound, presumably *l*(+)-threonine; its Bz_1 derivative, m.p. 151°, has $[\alpha]_D^{25} +25.1^\circ$ in EtOH .

H. W.

Synthesis of β -hydroxyleucine [α -amino- β -hydroxyisobutylacetic acid] and of β -hydroxy-norleucine [α -amino- β -hydroxy-*n*-hexoic acid]. E. ABDERHALDEN [with, in part, F. W. ZIESECKE and A. BAHN] (Z. physiol. Chem., 1938, 251, 164–170).—Addition of Br to *n*-hexoic acid and red P and treatment of the product with EtOH gives *Et* α -bromohexoate, b.p. 87–89°/vac., transformed by boiling NPhEt_2 into *Et* Δ^a -hexenoate, b.p. 59–63°/vac., which with $\text{Hg}(\text{OAc})_2$ in NaOH affords *Et* α -bromomercuri- β -methoxy-*n*-hexoate, an oil. This is converted by Br in CHCl_3 into *Et* α -bromo- β -methoxy-*n*-hexoate, b.p. 108–110°/12 mm., whence α -bromo- β -methoxy-*n*-hexoic acid, transformed by NH_3 at 37° into β -methoxynorleucine, m.p. 231° (decomp.), demethylated by HBr (*d* 1.49) to *r*- α -amino- β -hydroxy-*n*-hexoic acid (I) (β -hydroxynorleucine), m.p. 245–246°, reduced by P and HI (*d* 2) at 140–150° to *dl*-norleucine. (I) gives a *phenylcarbamate*, $\text{C}_{13}\text{H}_{18}\text{O}_4\text{N}_2$, m.p. 160–163°, a *phenylhydantoin* derivative, $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2$, m.p. 157–159°, and α -benzamido- β -hydroxy-*n*-hexoic acid, m.p. 185–186°; a Bz_2 derivative could not be obtained. A similar series of changes starting from isohexoic acid gives successively *Et* α -bromoisohexoate, b.p. 62°/14 mm., *Et* γ -methyl- Δ^a -pentenoate, b.p. 56.5–60°/vac., *Et* α -bromomercuri- β -methoxy- γ -methyl-*n*-valerate, *Et* α -bromo- β -methoxy- γ -methyl-*n*-valerate, b.p. 104–108°/13 mm., α -bromo- β -methoxy- γ -methyl-*n*-valeric acid, and α -amino- β -methoxy- γ -methyl-*n*-valeric acid (β -methoxyleucine), m.p. 256–258°. The last-named compound is demethylated by boiling HBr (*d* 1.49) to α -amino- β -hydroxy- γ -methyl-*n*-valeric acid (II) (β -hydroxyleucine), m.p. 242–244°, which is reduced to leucine. (II) gives a *phenylcarbamate*, $\text{C}_{13}\text{H}_{18}\text{O}_4\text{N}_2$, m.p. 198°, a *phenylhydantoin*,

$C_{15}H_{16}O_3N_2$, m.p. 197—200°, and an ill-defined *Bz* derivative.
H. W.

α -Sulphonyl- and $\alpha\alpha$ -disulphonyl-amides.
E. L. D'OUVILLE and R. CONNOR (J. Amer. Chem. Soc., 1938, 60, 33—36).—*p*- $C_6H_4MeSO_2Na$ and the appropriate α -chloro- or α -bromo-amide in hot EtOH give α -*toluenesulphonyl-acet*-, m.p. 166—167°, *-propion*-, m.p. 168—168.5°, and *-n-butyr-amide* (I), m.p. 175—175.5°. $CH_2Cl\cdot CO\cdot NH_2$ or $CHCl_2\cdot CO\cdot NH_2$ and Na mercaptides in EtOH at $\geq 0^\circ$ (to avoid oxidation by the Cl) give α -*n-butyl*-, m.p. 57—58°, α -*benzyl*-, m.p. 97—98°, $\alpha\alpha$ -*di-n-butyl*-, m.p. 104.5—105°, and $\alpha\alpha$ -*di-p-tolyl-thiolacetamide*, m.p. 172.5—173.5°, oxidised by H_2O_2 to α -*n-butane*-, m.p. 119—119.5°, α -*toluene- ω* -, m.p. 178.5—179°, $\alpha\alpha$ -*di-n-butane*-, m.p. 180.5—181.5°, and $\alpha\alpha$ -*di-p-toluene-sulphonylacetamide*, m.p. 195—196° [hydrolysed by aq. NaOH to $CH_2(SO_2\cdot C_6H_4Me)_2$]. The appropriate alkyl bromide, alkanesulphonylacetamide, and NaOEt afford (I), α -*p-toluenesulphonylisohexoamide*, m.p. 151.5—152°, α -*n-butane*-, m.p. 125—125.5°, and α -*toluene- ω -sulphonyl-n-butylamide*, m.p. 196—198°. The $(RSO_2)_2$, but not the RSO_2 , compounds dissolve in aq. Na_2CO_3 . Some of the products are hypnotics.
R. S. C.

Relationship between taste and constitution of dihydrazides of alkylmalonic acids and their derivatives. J. J. BLANKSMA and H. DE GRAFF (Rec. trav. chim., 1938, 57, 3—12).—By condensation of the appropriate hydrazide with aldehydes and ketones, the following are prepared. Malonodihydrazide (I) yields *malonodi-isopropylidene*-, m.p. 180°, *-benzylidene*-, *-anisylidene*-, m.p. 221°, and *-piperonylidene-hydrazide*, m.p. 223°. Methylmalonodihydrazide (II) yields *methylmalonodi-isopropylidene*-, m.p. 178°, *-benzylidene*-, *-anisylidene*-, m.p. 241°, *-piperonylidene-hydrazide*, m.p. 247°. Ethylmalonodihydrazide (III) yields *ethylmalonodi-isopropylidene*-, *-benzylidene*-, *-anisylidene*-, and *-piperonylidene-hydrazide*, m.p. 223°. *n*-Propylmalonodihydrazide (IV) (Ac_2 derivative, m.p. 245°) yields *n-propylmalonodi-isopropylidene*-, *-benzylidene*-, m.p. 245°, *-anisylidene*-, m.p. 244°, and *-piperonylidene-hydrazide*, m.p. 244°. *iso*-Propylmalonodihydrazide (V), m.p. 214° (Ac_2 derivative, m.p. 254°), yields *isopropylmalonodi-isopropylidene*-, m.p. 204°, *-benzylidene*-, m.p. 261°, *-anisylidene*-, m.p. 278°, and *-piperonylidene-hydrazide*, m.p. 283°. *n*-Butylmalonodihydrazide (VI), m.p. 142°, yields *n-butylmalonodi-isopropylidene*-, m.p. 110°, *-benzylidene*-, m.p. 239°, *-anisylidene*-, m.p. 242°, and *-piperonylidene-hydrazide*, m.p. 253°. Benzylmalonodihydrazide (VII) (Ac_2 derivative, m.p. 246°) yields *benzylmalonodi-isopropylidene*-, m.p. 168°, *-benzylidene*-, m.p. 242°, *-anisylidene*-, m.p. 248°, and *-piperonylidene-hydrazide*, m.p. 244°. (I) to (VII) possess sweet tastes, the sweetness diminishing in numerical order. Acetylation decreases greatly or eliminates the sweet taste. Condensation of the hydrazino-residue with aldehydes and ketones causes disappearance of the sweet taste and produces bitterness. *Et_2* hydrazinomalonate, m.p. 87°, and *hydrazinomalonodihydrazide*, m.p. 175°, are tasteless.
E. I.

Coloured free radical derived from cyanogen.
E. V. ZAPPI and R. LABRIOLA (Bull. Soc. chim.,

1938, 5, [v], 27—29).—When solutions of CNI in Et_2O and of NaOEt are mixed in N_2 a yellow coloration appears, disappearing on admission of O_2 with formation of a white ppt. of NaI, NaCN, Na_2CO_3 , and NH_4 salts; also present are $MeCHO$, $CO(NH_2)_2$, $CHCl_3$, and $CN\cdot NH_2$. This reaction is not shown by Na, K, or Zn with CNI nor by NaOEt with MeCN, $CHPh_2\cdot CN$, CNCl, CNBr, or compounds containing positive I. A primary or sec. alcohol must be present. It is assumed that $I\cdot C\dot{N}$ reacts with NaOEt to give $I\cdot CNa\cdot NNa$, EtOH, and $MeCHO$. $CNa\cdot I\cdot NNa$ decomposes into NaI and the coloured radical $\dot{C}NNa$ (or $\dot{C}NNa$) which either passes into NaCN or with O_2 gives its peroxide $(CNNa)_2O_2$. This is either hydrolysed to $NH_2\cdot CO_2H$ and NaOH, passing into Na_2CO_3 and NH_3 , or reacts with NH_3 to give $CO(NH_2)_2$ and NaOH.
E. G. B.

Photolysis of azomethane.—See A., I, 153.

Phosphonic acids and their alkyl esters from $\alpha\beta$ -unsaturated ketones. L. R. DRAKE and C. S. MARVEL (J. Org. Chem., 1937, 2, 387—399).—Ketones $CHR\cdot CH\cdot CO\cdot R$ (R = alkyl or aryl) add PCl_3 in Ac_2O to give phosphonyl chlorides $CHR\cdot CH\cdot CR$ (I) $PO(X)-O$ ($X = Cl$), hydrolysed to ketophosphonic acids $PO(OH)_2\cdot CHR\cdot CH_2\cdot CO\cdot R$ (II). (I) with long-chain aliphatic alcohols $R'\cdot OH$ give cryst. alkali-insol. mono-esters $OR'\cdot PO(OH)\cdot CHR\cdot CH_2\cdot CO\cdot R$ (III) in which the acidic properties of the OH are masked by the R' . Mesityl oxide (IV) with PCl_3 in Ac_2O gives, after hydrolysis of the reaction mixture, δ -methylpentan- β -one- δ -phosphonic acid (V), m.p. 62—63°, or with the appropriate alcohol the *Bu*, b.p. 82—100/ 2×10^{-4} mm., and *n-decyl*, b.p. 104—145°/ 1×10^{-4} mm., esters of (V). With tetradecanol (VI) and hexadecanol, the corresponding alkyl chloride and $CMe_2\cdot CH\cdot CMe$ are obtained. This indicates that $PO(OH)-O$ (III) are formed through (I) ($X = OR'$), giving with the liberated HCl, $R'\cdot O\cdot PO(Cl)\cdot CHR\cdot CH_2\cdot CO\cdot R$, which with more $R'\cdot OH$ gives (III). Heating of (III) may lead to (I) ($X = OH$) (VII) and $R'\cdot Cl$. Alternatively (VII) may be the first product, passing into (III) by addition of $R'\cdot OH$. The following $\alpha\gamma$ -diphenylpropan- α -one- γ -phosphonates are described. *n-Decyl*, m.p. 107—108° (reduction with H_2 —Pt gives $\alpha\gamma$ -diphenylpropan- γ -phosphonic acid, m.p. 168—171°); *n-dodecyl*, m.p. 110—113°; *n-tetradecyl*, m.p. 112—114°; *n-hexadecyl*, m.p. 108—110°; *n-octadecyl*, m.p. 105—109°; *n-octadec-1-enyl*, m.p. 89—90°. $(CHBz)_2$ with PCl_3 gives, after hydrolysis, $\alpha\delta$ -diphenylbutane- $\alpha\delta$ -dione- β -phosphonic acid, m.p. 183—185° (decomp.). With decanol (VIII) or (VI), the cyclic compound, m.p. 197—198°, corresponding with (VII), is produced. $PBuCl_2$, b.p. 157—150°/750 mm., reacts like PCl_3 and with (IV) and $CHPh\cdot CHBz$ (IX) yields respectively the *Bu* derivative of (V) (*K* salt) and *n-butyl- $\alpha\gamma$ -diphenylpropan- α -one- γ -phosphonic acid*, m.p. 191—193°. $PCl(OPh)_2$ in the same way adds to (IV) yielding the Ph_2 ester of (V), b.p. 136—150°/ 8×10^{-4} mm., and to $CHAc\cdot CH_2$ (X) yielding *Ph_2 butan- β -one- δ -phosphonate*, b.p. 95—112°/ 3×10^{-4} mm. No phosphonic acid can be isolated from (X) and PCl_3 , but with (VIII) the

reaction mixture yields *di-n-decyl butan-β-one-δ-phosphonate*, b.p. 120—170°/1 × 10⁻⁴ mm. PCl₃ does not add to CHPh:CH·CO₂Ph nor AsCl₃ to (IX).

Phosphonic acids CHEtR·CH(PO₃H₂)·CH₂·CO·R' are prepared from PCl₃ and ketones CHEtR·CH:CH·CO·R'. The following are described: Δ⁷-ε-ethylnonen-β-one, b.p. 163—167°/2 mm.; Δ⁰-κ-ethyltetradecen-η-one, b.p. 130—134°/3—4 mm.; Δ⁸-γ-ethyldodecen-ζ-one, b.p. 97—103°/2 mm.; ε-ethylnonan-β-one-δ-, m.p. 66—69°, ε-ethylheptan-β-one-δ-, dark brown oil, γ-ethylundecan-ζ-one-δ-, m.p. 60—65°, and ι-ethyltridecan-ζ-one-θ-, dark brown oil (Na salt), -phosphonic acid; γ-ethyldodecan-ζ-one-δ-, dark oil, and Δ⁸-γ-diethylundecen-ζ-one-θ-, yellow oil, -phosphonic anhydride. E. G. B.

Organo-boron compounds. [I.] Study of reaction mechanisms. Primary aliphatic boronic acids. H. R. SNYDER, J. A. KUCK, and J. R. JOHNSON. **II. Reducing action of some organo-boric acids.** J. R. JOHNSON, M. G. VAN CAMPEN, jun., and O. GRUMMITT. **III. Reactions of tri-*n*-butylborine.** J. R. JOHNSON, H. R. SNYDER, and M. G. VAN CAMPEN, jun. **IV. Reaction of tri-*n*-butylborine with peroxides and with oxygen. Mechanism of autoxidation.** J. R. JOHNSON and M. G. VAN CAMPEN, jun. (J. Amer. Chem. Soc., 1938, 60, 105—111, 111—115, 115—121, 121—124).—I. Org. B compounds are investigated because they may resemble the hypothetical active forms of C compounds owing to the open sextet of electrons of the B. Alkane-boronic acids, Alk·B(OH)₂, are best prepared from pure Me₃BO₃ and the Grignard reagent in Et₂O under pure N₂ at -75°. Thus are obtained *n*-butane- (I), m.p. 92—94° [Na salt (II), +0.5H₂O, over P₂O₅ gives the salt, Na₂(BuBO)₂O], *n*-hexane-, m.p. 88—90°, *n*-pentane-, m.p. 93—94°, *n*-propane-, m.p. 106—107°, *isobutane*-, m.p. 106—112°, and impure *n*-tetradecane-α-boronic acid, m.p. indefinite. These m.p. are obtained only by drying over 65% H₂SO₄ in N₂; the acids frequently separate as hydrates and, when dried as usual, pass into oxides, RBO. These acids resemble the aromatic boronic acids only in being oxidised by H₂O₂ to the alcohol and H₃BO₃ and in thermal decomp.; when heated, (II) gives C₄H₁₀. The acids are inert to aq. Hg, Cd, Zn, and Cu halides, conc. aq. alkalis, and 40% HBr or HI at 100°. They readily autoxidise, yielding first OR·B(OH)₂ and then by hydrolysis ROH and H₃BO₃. With ammoniacal AgNO₃ they give 1 atom of Ag and the hydrocarbon, R₂; thus (I) gives 70—80% of *n*-C₃H₁₈. They are extremely weak acids and cannot be titrated with alkali even in presence of mannitol. They readily lose H₂O over P₂O₅ or H₂SO₄, when heated alone in vac., or when treated with SOCl₂, yielding trimeric oxides; *n*-butyl-, b.p. 138°/18 mm., and *n*-hexyl-boron oxide, b.p. 178—182°/24 mm., are thus obtained. These add H₂O exothermally to regenerate the acid; the former gives a ppt. with dry NH₃ in Et₂O and reacts exothermally with EtOH, MeOH, NHPH·NH₂, and bases, and with MgBu⁺Br at -65° gives much BBU(OH)₂ and some BBU⁺₃. B is determined in the acids by fusion with Na₂O₂ in a Parr bomb and in other compounds by oxidation with alkaline H₂O₂ and subsequent fusion

at 130—150°; in both cases the H₃BO₃ formed is finally titrated. The stability of the oxides is explained by resonance and an electronic explanation is suggested for the resemblance of the acids to aldehydes. *sec.*- and *tert.*-Alkane- and *cycloalkane*-boronic acids differ from those described above.

II. Marked differences in the behaviour of aliphatic and aromatic boronic acids are noted. Aromatic boronic acids are mainly hydrolysed by ammoniacal AgNO₃, only a trace of Ag being pptd. Toluene-α-boronic acid, m.p. 104°, is very readily autoxidised, even in presence of H₂O, which inhibits oxidation of BBu(OH)₂; it is stable to hot H₂O or 5% HCl, but with hot 5% NaOH gives quantitatively PhMe and H₃BO₃; with ammoniacal AgNO₃ it gives Bz₂ and Ag. *iso*Butane-β-boronic acid, m.p. 103—105° (decomp.), with SOCl₂ gives *B Bu'* oxide, b.p. 66—68°/5 mm., m.p. 20°, and is also unusually readily autoxidised; with ammoniacal AgNO₃ it gives Ag and Bu'OH with only traces of C₂Me₆ and a little *iso*-C₄H₈ and *iso*-C₄H₁₀. *Furan-2-boronic acid*, dimorphic, m.p. 110° (decomp.) and 121—122°, can be titrated in presence of mannitol; it is stable in air; with aq. or ammoniacal AgNO₃ it gives the Ag salt, which decomposes, when warmed, to yield furan and no Ag; with aq. HgCl₂ it gives 2-chloromercurifuran, with CuCl₂ or CuBr₂ it gives the Cu^I halide and 2-halogenofuran, and with I gives 2-iodofuran. *Thiophen-2-boronic acid*, m.p. 134—135°, resembles the furan-acid in being titratable and in its reactions with AgNO₃, HgCl₂, CuBr₂, and I; with Br it gives 2-bromothiophen and with warm *n*-HCl or boiling 20% NaOH yields thiophen. The instability of the alkyl compounds to Ag₂O solutions may be due to the non-formation of Ag salts, and the formation of hydrocarbons, R₂, may occur by way of AgAlk.

III. Alkylborines can react only by the open sextet of the B functioning as an electron-acceptor to give complexes, X-Y→BR₃, or by the alkyl group forming a H-bridge, e.g., X-Y→H·CH₂·BR₂. Addition reactions are discovered and interpreted by the former reaction mechanism. *Tri-n-butylborine*, b.p. 108—110°/20 mm., is obtained in 80% yield from MgBuBr and BF₃ or in 50% yield from Me₃BO₃ and an excess of MgBuBr. It oxidises rapidly and exothermally in air and ignites when poured on to cotton. It does not react with bases, *p*-C₆H₄Me·SO₂H, or *p*-C₆H₄Me·SH, but gives a red colour with picric acid. Quaternary borates, M⁺[BR₄]⁻, could not be isolated, but their existence is proved. Thus, BBU⁺₃ reacts exothermally with 2 mols. of MgPhBr in Et₂O with formation of two layers, the lower of which contains [BPhBu⁺₃]⁻[MgPh(Et₂O)_n]⁺, since with H₂O it gives slowly C₆H₆ and BBU₃ and with PhNCO gives incompletely NHPHBz; BBU⁺₃ reacts exothermally with 1 mol. of MgPh₂ in Et₂O to give two layers, the lower of which contains the complex borate. In Et₂O BBU₃ also reacts exothermally with LiPh, LiBu⁺, and MgBu⁺Br without separation into layers, but not with ZnBu⁺₂. Failure hitherto to report such reactions is due to use of hydrocarbon solvents, since solvation with Et₂O appears to be essential for their occurrence. With 48% aq. HBr BBU₃ gives 1 mol. each of *n*-C₄H₈ and BBU₂Br; the bromide is at once hydrolysed to di-*n*-butylborinic acid, which is isolated

by dehydration (distillation in vac. in N_2) to *di-n-butylboron oxide*, $(BBu_2)_2O$, b.p. $136^\circ/12$ mm. This oxide is rapidly oxidised and ignites in air if in a thin film; it is unaffected by cold aq. alkali; when heated with BuOH with continuous removal of H_2O it gives *Bu^a di-n-butylborinate*, $BBu_2 \cdot O Bu^a$, b.p. $110-111^\circ/19$ mm., which reacts incompletely with $MgPhBr$ to yield a little $BPh(OH)_2$. With anhyd. HBr at $55-60^\circ$ BBu_3 gives 1 mol. each of C_4H_{10} and *B Bu^a bromide*, b.p. $44^\circ/4$ mm., stable to Ag and amalgams, but readily hydrolysed to $BBu_2 \cdot OH$ by H_2O . BBu_3 is stable to I or Br in CCl_4 , but with Br alone a complex reaction occurs: fission gives BuBr and BBu_2Br , and then *B Bu^a dibromide*, $BBu^a Br_2$, b.p. $65^\circ/23$ mm.; simultaneously some substitution in the Bu occurs, liberating HBr, which in part reacts with BBu_3 to give C_4H_{10} and BBu_2Br . With $Bu^v OCl$ (3 mols.), even at -80° , BBu_3 gives 33% of $Bu^v Cl$, indicating the reaction, $BBu^a_3 + Bu^v OCl \rightarrow BBu^a_2 \cdot O Bu^v + Bu^v Cl$, but some substitution also occurs and elimination of HCl leads to some *butenyl di-n-butylborinate*, b.p. $70-71^\circ/4$ mm., and probably some $B(C_4H_7)_3$. It is assumed that, when HBr reacts with BBu_3 , co-ordination of the Br and B increases the mobility of a Bu, which then undergoes an irreversible $\alpha \rightarrow \gamma$ shift to yield C_4H_{10} . Similarly, the O of $Bu^v OCl$ co-ordinates with the B and $Bu^v Cl$ is split off by the $\alpha \rightarrow \gamma$ shift. Failure of BBu_3 to lose >1 Bu to Br and the stability of BBu_2Br to HBr (experimentally proved) are attributed to a resonance

effect, $BBu_2-Br \rightleftharpoons \bar{B}Bu_2=Br^+$, by which unshared electrons of the Br partly satisfy the acceptor activity of the B and thus diminish its affinity for an external donor mol. so that co-ordination does not now supply sufficient energy to the Bu to enable the $\alpha \rightarrow \gamma$ shift to occur. Bromination by Br may be due to activation of CH_2 by the neighbouring B or of Br mols. by BBu_3 .

IV. Bz_2O_2 and BzO_2H in $CHCl_3$ react readily with BBu^a_3 , e.g., $BBu_3 + 3BzO_2H \rightarrow B(OBu)_3 + 3BzOH$, and subsequent treatment with cold alkali gives $3BuOH$ and H_3BO_3 (almost quantitatively with BzO_2H). In presence of H_2O BBu_3 absorbs 0.5 O_2 to give 92% of $BBu^a_2 \cdot O Bu^a$, b.p. $120-121^\circ/24$ mm. (see above), the reaction being interpreted thus: $BBu_3 + O_2 \rightarrow Bu_3B \leftarrow O:O$; $BBu_3O_2 + BBu_3 \rightarrow 2BBu_2 \cdot O Bu$. In dry air 1 O_2 is absorbed and the product obtained is pure *Bu^a n-butane- α -boronate*, $BBu(OBu)_2$, b.p. $110-111^\circ/24$ mm.; this is similarly interpreted, the intermediate $BBu_2 \cdot O Bu$ co-ordinating with O_2 when H_2O is absent. The inability of $BBu_2 \cdot O Bu$ to oxidise further in H_2O is due to the B-O linking and may be connected with the ability of the boronic acids to form hydrates. Ease of cleavage of alkyl decreases in the following series: $BR_3 > BR_2X > BRX_2$, X being Br, OH, or OAlk; this is explained by the resonance theory elaborated above for the reaction with Br. BzO_2H and H_2O_2 remove all three, Br and dry O_2 remove two, and HBr and moist O_2 remove one alkyl from the B. R. S. C.

Compounds of bivalent platinum with α -alanine. A. A. GRÜNBERG and L. M. VOLSCHTEIN (Bull. Acad. Sci. U.R.S.S., 1937, 885-905; cf. A., 1937, II, 330).—The compound of $[PtAn_2]$ (HAn = alanine) reported by Ley and Ficken (A., 1912, i, 243) is a

non-electrolyte with a *trans*-configuration. The compound $[PtAnG]$ (HG = glycine), with a *trans*-configuration, has been obtained by the reaction $K[PtCl_2An] + HG \rightarrow [PtAnG] + KCl + HCl$. The compounds $[PtCl_2, 2HAn]$, $[PtCl_2, HAn, HG]$, $[Pt, 2NH_3, 2HAn]Cl_2$, $[Pt, 2NH_3, HAn, HG]Cl_2$, $[Pt, 2T, 2HAn]Cl_2$ ($T = CS(NH_2)_2$), $[Pt, 2T, HAn, HG]Cl_2$, $[Pt, 2NH_3, An_2]$, $[Pt, 2NH_3, An, G]$, $[Pt, 2T, An_2]$, and $[Pt, 2T, An, G]$ have been prepared. Compounds of the formula $M_2[PtAn_4]$ could not be obtained in the solid state owing to their high solubility, but the compound $[Pt, 4HAn, Cl_2]Cl_2$ has been prepared. R. C.

Hydroxy-compounds of quadrivalent platinum.—See A., I, 94.

Vapour-phase reactions of cyclopropane with iodine and bromine. R. A. OGG, jun., and W. J. PRIEST (J. Amer. Chem. Soc., 1938, 60, 217-218).—*cyclo*Propane and I at $250^\circ/300$ mm. give mainly $CH_2(CH_2I)_2$; the reaction is unaffected by light and so I atoms play no part. In light at room temp. Br gives rapidly $CH_2(CH_2Br)_2$ and 2% of HBr; in the dark at 220° reaction is as fast as that with I, but much HBr is formed. Gaseous HCl, HBr, and HI react only slightly at 300° , but at room temp. HCl reacts slowly, doubtless by a complex mechanism. All reactions were effected in Pyrex glass.

R. S. C.

Organic reactions with boron fluoride. XVIII.

Reaction of ethers with benzene. M. J. O'CONNOR and F. J. SOWA (J. Amer. Chem. Soc., 1938, 60, 125-127).—Reaction of ethers with C_6H_6 in presence of BF_3 occurs by intermediate olefine formation, since $(n-C_5H_{11})_2O$ gives $CHPhMePr^a$ (29.6% with 40.4% of polyamyl derivatives) and $(iso-C_5H_{11})_2O$ gives *tert*-amylbenzene (12.4% with 32% of polyamyl derivatives). Pr^a_2O and $(CH_3Ph)_2O$ react vigorously with C_6H_6 , forming $PhPr^a$ and CH_2Ph , respectively, also formed from $PhOPr^a$ and $CH_2Ph \cdot OEt$ (which react explosively), respectively. Et_2O and $(C_5H_{11})_2O$ react only at high temp. and pressure. Di- (mostly *p*- with very little *o*-) and poly-alkyl compounds are usually also formed. BF_3 causes reaction by co-ordination with the ethereal O and thus weakening the C-O linking. Some dehydration of the alcoholic fission product to an olefine and consequent further reaction with C_6H_6 occurs. R. S. C.

Synthesis of *o*- and *m*-propenyltoluene and *o*-allyltoluene. R. J. LEVINA and I. C. GRINBERG (J. Gen. Chem. Russ., 1937, 7, 2306-2308).—The b.p., *n*, and *d* of *o*-, *m*-, and *p*- C_6H_4MeBr , *o*-, *m*-, and *p*-tolylethylcarbinol, *o*-, *m*-, b.p. $94-5^\circ/22$ mm., and *p*-propenyltoluene, and *o*-, *m*-, and *p*-allyltoluene are tabulated. R. T.

Salts of nitro-compounds. II. Reaction of the silver salt of phenylnitromethane with diphenylbromomethane. G. B. BROWN and R. L. SHRINER (J. Org. Chem., 1937, 2, 376-380; cf. A., 1937, II, 490).— $CHPhAg \cdot NO_2$ (I) with $CHPh_2Br$ (II) yields a mixture of $CHPh_2 \cdot CHPh_2$ (III) and α -($CHPh \cdot NO_2$)₂ (IV) by two simultaneous couplings. Thus (I) decomposes into (IV) and free Ag, which then couples two mols. of (II) yielding (III). (I) in

C_6H_6 yields on shaking β -(CHPh \cdot NO $_2$) $_2$ (V), also formed by action of NO $_2$ on stilbene or of I on CHPhNa \cdot NO $_2$. (IV) and (V) both yield triphenylisoxazole by action of alkali.

E. G. B.

Mesitylene derivatives. III. Reaction of di-(2:4:6-trimethylphenyl)methyl chloride (dimesitylmethyl chloride) with molecular silver. W. T. NAUTA and P. J. WUIS (Rec. trav. chim., 1938, 57, 41—60; cf. A., 1937, II, 332).—Di-(2:4:6-trimethylphenyl)methyl chloride (I) in C_6H_6 with Ag in N $_2$ gives an orange colour which rapidly changes to a stable red-violet. The colour of this solution, which does not obey Beer's law on dilution, and is destroyed by O $_2$, is considered to be due to the dimesitylmethyl radical. Attempts to isolate tetramesitylthane (II) from the solution give mixtures, m.p. 140—190°, containing dimesitylmethane; (I) heated in N $_2$ or with C $_5$ H $_5$ N yields only resinous material, and no (II). (I) with Ag in C_6H_6 in O $_2$ (absorption of 3 O) yields 2:4:6-trimethylphenol (III) and benzaldehyde, dimesityl ketone, and a substance (C $_{19}$ H $_{23}$ O) $_n$, m.p. 257° (decomp.), which with Zn-AcOH yields a little (III). The solution of (I) in C_6H_6 with Ag absorbs NO with formation of a blue-green colour, rapidly changing to yellow, and from this solution dimesitylcarbinol is isolated.

E. I.

Magnetic investigation of $\omega\omega'$ -phenylpolyenes.—See A., I, 128.

Syntheses with *p*-cyclohexylbenzyl chloride. D. BODROUX and R. THOMASSIN (Compt. rend., 1937, 205, 1417—1418).—*p*-cyclohexylbenzyl chloride (I) reacts readily with Mg in presence of Et $_2$ O and the product is transformed by O $_2$ and CO $_2$ into *p*-cyclohexylbenzyl alcohol, m.p. 40° (yield 34%), and *p*-cyclohexylphenylacetic acid, m.p. 78.5° (yield 55% if the gas is used and 60% if the solid is employed), respectively. *p*-cyclohexyltoluene and di-*p*-cyclohexyldibenzyl, m.p. 148—149° [also from (I) and Na in boiling Et $_2$ O], are formed as by-products. Oxidation of (I) by boiling dil. Cu(NO $_3$) $_2$ or, preferably, Pb(NO $_3$) $_2$ affords *p*-cyclohexylbenzaldehyde, b.p. 158—160°/10 mm. (corresponding anil, m.p. 117—118°), with a considerable proportion of *p*-cyclohexylbenzoic acid, m.p. 197—198°.

H. W.

Configurational effects in the solvolytic reactions of α -phenylethyl chloride.—See A., I, 86.

2-Ethyl-naphthalene. G. LÉVY (Ann. Chim., 1938, [xi], 9, 5—87).—2-C $_{10}$ H $_8$ ·Ac, obtained by addition of AlCl $_3$ to C $_{10}$ H $_8$ and AcCl in PhNO $_2$ at -5° to 0°, is reduced by H $_2$ in presence of Ni-pumice at 200° to 2-C $_{10}$ H $_7$ ·Et (I), b.p. 257—258° (corr.)/760 mm., m.p. -7° to -6.5°, purified through the picrate, m.p. 76.5—77°; it is accompanied by its H $_4$ -derivative, which is readily dehydrogenated by S to (I). Clemmensen's method gives unsatisfactory results probably owing to polymerisation of 2-vinylnaphthalene formed intermediately. Reduction of 8-keto-2-ethyl-5:6:7:8-tetrahydronaphthalene (II) [semicarbazone, m.p. 197° (corr.)] by Zn-Hg and 5N-HCl gives 2-ethyl-5:6:7:8-tetrahydronaphthalene (III), b.p. 239—239.5° (corr.)/736 mm. 1-Keto-2-

ethyl-1:2:3:4-tetrahydronaphthalene (IV), b.p. 109°/13 mm. [semicarbazone, m.p. 207.5° (corr.)], is converted similarly (with subsequent treatment with Raney Ni) into 2-ethyl-1:2:3:4-tetrahydronaphthalene (V), b.p. 235—235.5° (corr.)/731 mm. Hydrogenation of (I) in presence of Ni prepared at 360° leads exclusively to (III); in presence of Ni obtained at 280° 2-ethyldecahydronaphthalene (VI) appears to result in considerable amount with a mixture of (III) and (V). Reduction by Na in boiling isoamyl alcohol gives only 2-ethyldihydronaphthalene, b.p. 245° (corr.)/760 mm. (non-cryst. dibromide), whereas use of Ni prepared at 250° leads to (VI), b.p. 222° (corr.)/760 mm. Hydrogenation of (V) at 160° in presence of Ni obtained at 250° gives (VI), b.p. 92°/13 mm., 222° (corr.)/760 mm. (probably a mixture of isomerides).

Addition of 100% HNO $_3$ to (I) in AcOH at 3° to 10° gives preponderantly a cryst. NO $_2$ -derivative (VII), m.p. 49.5—50°, reduced to an amine (VIII), m.p. 25—28° (Ac derivative, m.p. 156.5°), and a non-characterised isomeric NO $_2$ -compound, transformed into an amine (IX) (Ac compound, m.p. 148.5—149°). (VIII) is transformed by dil. acid under pressure or by diazotisation and subsequent treatment with steam into 2-ethyl-1-naphthol (X), m.p. 69.5—70° (picrate, m.p. 119.5°). (VII) is therefore 2-nitro-1-ethylnaphthalene. CH $_2$ Ph·CH $_2$ Br (prep. from CH $_2$ Ph·CH $_2$ ·OH described) and CHNa(CO $_2$ Et) $_2$ yield Et $_2$ β -phenylethylmalonate, b.p. 156°/4 mm., which with EtBr gives Et $_2$ β -phenyldiethylmalonate, b.p. 151°/3 mm., whence successively β -phenyldiethylmalonic acid, m.p. 129°, and γ -phenyl- α -ethyl-n-butyric acid, b.p. 180°/16 mm., m.p. 104°. This is converted by cold SOCl $_2$ into γ -phenyl- α -ethyl-n-butyryl chloride, b.p. 142°/15 mm., cyclised by AlCl $_3$ in light petroleum to 1-keto-2-ethyl-1:2:3:4-tetrahydronaphthalene (see above), dehydrogenated by Se at 300—360° to (X). (IX) is hydrolysed by dil. H $_2$ SO $_4$ at 200° into an ethylnaphthol (XI), m.p. 56.5—57° [picrate, m.p. 131—131.5° (corr.)]. CH $_2$ Ph·CHO and MgEtBr afford α -phenylbutan- β -ol, b.p. 106—107°/13 mm., readily converted into β -bromo- α -phenylbutane, b.p. 109—110°/pressure, which does not appear to react with CHNa(CO $_2$ Et) $_2$. Benzyl-ethylmalonic acid is decarboxylated to α -benzyl-butyric acid, b.p. 174°/15 mm., the isoamyl ester, b.p. 154°/15 mm., of which is reduced by Na in boiling isoamyl alcohol to β -benzyl-n-butyl alcohol, b.p. 142—144°/16 mm. β -Benzyl-n-butyl bromide, b.p. 131°/14 mm., is transformed into the corresponding nitrile, b.p. 142°/13 mm., hydrolysed by conc. HCl at 120—130° to β -benzyl-n-valeric acid, b.p. 175°/13 mm. The chloride of this is cyclised by AlCl $_3$ to 4-keto-2-ethyl-1:2:3:4-tetrahydronaphthalene, b.p. 145°/14 mm. [semicarbazone, m.p. 171.5° (corr.)], dehydrogenated by Se to the very unstable 2-ethyl-4-naphthol, b.p. 170°/11 mm., m.p. 50.5—51° [picrate, m.p. 145° (corr.)]. Addition of AlCl $_3$ to a mixture of succinic anhydride, PhEt, and C $_6$ H $_6$ yields β -p-ethylbenzoylpropionic acid, m.p. 102—103°, reduced (Clemmensen) to γ -p-ethylphenyl-butyric acid (XII), m.p. 70°, the chloride, b.p. 143—145°/18 mm., of which is cyclised to 8-keto-2-ethyl-5:6:7:8-tetrahydronaphthalene, b.p. 152—154°/13 mm.

18 mm. (see above); dehydrogenation of this gives (XI). Alternatively, a mixture of PhEt, trioxymethylene, and ZnCl_2 is transformed by HCl into *p*-ethylbenzyl chloride, b.p. 102–103°/19 mm., which with HCN or $\text{Et}_2\text{C}_2\text{O}_4$ gives Et_2 *p*-ethylbenzylmalonate, b.p. 175–178°/3 mm. The corresponding acid, m.p. 144–145°, is decarboxylated to β -*p*-ethylphenylpropionic acid, m.p. 73°, the *amyl ether*, b.p. 169–171°/12 mm., of which is reduced to γ -*p*-ethylphenylpropyl alcohol, b.p. 140°/12 mm. (*phenylurethane*, m.p. 56°). This is transformed through the bromide and cyanide, b.p. 154–155°/15 mm., into (XII).

Sulphonation of (I) gives 2 : 6- $\text{C}_{10}\text{H}_6\text{Et}\cdot\text{SO}_3\text{H}$ (very sparingly sol. *Ba* salt), the *Na* salt (XIII) of which is transformed by PCl_5 into 2-ethylnaphthalene-6-sulphonyl chloride, m.p. 69–69.5°, whence the corresponding amide, m.p. 190–191° (corr.). Fusion of (XIII) with NaOH at 270–300° affords 2-ethyl-6-naphthol (XIV), m.p. 97–98° [*picrate*, m.p. 106–107°; *Me ether* (XV), m.p. 58°]. *p*-Methoxybenzyl chloride (XVI), b.p. 120°/18 mm., is condensed with difficulty with $\text{CETNa}(\text{CO}_2\text{Et})_2$ to Et_2 *p*-methoxybenzylethylmalonate, b.p. 161°/2 mm.; the corresponding acid, m.p. 131.5–132.5°, is decarboxylated to α -*p*-methoxybenzyl-*n*-butyric acid, b.p. 195°/13 mm., the *amyl ester*, b.p. 188–189°/13 mm., of which is reduced to β -*p*-methoxybenzyl-*n*-butyl alcohol, b.p. 165°/15 mm. Bromination of the alcohol gives only resins and it is therefore converted by SOCl_2 and NPhMe_2 into β -*p*-methoxybenzyl-*n*-butyl chloride, b.p. 160°/13 mm. This is transformed through the iodide, b.p. 165°/13 mm., into the nitrile, b.p. 172–175°/13 mm., hydrolysed to γ -*p*-methoxybenzyl-*n*-valeric acid, b.p. 205°/13 mm., the chloride, b.p. 175°/13 mm., of which is cyclised to 4-keto-6-methoxy-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 180°/13 mm. [*semicarbazone*, m.p. 171–172° (corr.)]. Reduction of the ketone yields 6-methoxy-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 148–153°/13 mm., readily dehydrogenated by S at 260° giving (XV), demethylated by boiling HI to (XIV).

(XVI) is converted by an excess of NaCN in dry COMe_2 into *p*-anisylacetonitrile, hydrolysed to the acid, m.p. 88°, the *amyl ester*, b.p. 134°/13 mm., of which is reduced to β -*p*-anisylethyl alcohol, m.p. 28°. The corresponding chloride is condensed with $\text{CETNa}(\text{CO}_2\text{Et})_2$ to Et_2 β -*p*-anisylethylethylmalonate, b.p. 200°/5 mm., hydrolysed to β -*p*-anisylethylethylmalonic acid, m.p. 122°. This is decarboxylated to α -*p*-anisylethyl-*n*-butyric acid, b.p. 212°/19 mm., the chloride, b.p. 177°/19 mm., of which is cyclised to 1-keto-7-methoxy-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 175°/17 mm., m.p. 46–46.5°. Reduction of the ketone (Clemmensen) yields 7-methoxy-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, dehydrogenated to 7-methoxy-2-ethylnaphthalene, m.p. 51–52°.

H. W.

Compound decomposing easily in the pure state under the catalytic influence of the container. S. C. J. OLIVIER and J. WIT (Rec. trav. chim., 1938, 57, 90–94).—Crude 2- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Br}$ (I) may be distilled without decomp. (155–180°/14 mm.), but on redistillation the pure (I) decomposes into HBr and a substance, $(\text{C}_{11}\text{H}_8)_n$, probably poly-

meric di-2-naphthylethylene. The decomp. is most rapid in soft glass, slowest in Pyrex, and is accelerated by pumice. The prep. from (I) of 2- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CN}$ (100%) and 2- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (>90%) is described. E. I.

Dissociable anthracene oxides. Photo-oxidation of anthracene. C. DUFRAISSE and M. GÉRARD (Bull. Soc. chim., 1937, [v], 4, 2052–2063; cf. A., 1935, 969, 1488; 1936, 1110).—When irradiated in CS_2 or CHCl_3 anthracene gives a photo-oxide, and when in C_6H_6 or Et_2O a polymeride. In $\text{CS}_2 + \text{Et}_2\text{O}$ both processes are inhibited. The possible mechanism of photo-oxidation through an intermediate dimeride is discussed on a steric basis; the intervention of a 9 : 10-diradical is considered unlikely. E. W. W.

Dissociable anthracene oxides. Question of monatomic meso-bridges. 9-Phenyl-9 : 10-dihydromesoanthracene and 2 : 5-diphenyl-3 : 4-benzthiophen. C. DUFRAISSE and D. DANIEL (Bull. Soc. chim., 1937, [v], 4, 2063–2070).—Bistrzycki's "9-phenyl-9 : 10-dihydromesoanthracene" (A., 1922, i, 268; cf. also A., 1924, i, 1333) is actually 2 : 5-diphenyl-3 : 4-benzthiophen (I), m.p. 118–119°, since it can be obtained from 2 : 5-diphenyl-3 : 4-benzfuran (II) (A., 1932, 1257) and P_2S_5 , and since absorption spectra of (I) and (II) show only normal differences between a thiophen and a furan. The pyrogenic formation of 9-phenylanthracene from (I) (Zn) is also observed with (II) and with $\text{o-C}_6\text{H}_4\text{Bz}_2$; at >400°, anthracene is formed.

E. W. W.

Phenanthrene derivatives. VIII. Hexa-arylethanes containing the phenanthrene nucleus. W. E. BACHMANN and M. C. KLOETZEL (J. Org. Chem., 1937, 2, 356–375).—The dissociation of hexa-arylethanes in solution is due to weakness of the C-C linking and to stability of the triarylmethyl radicals produced, and is accounted for by a combination of steric hindrance and resonance (cf. Bent *et al.*, A., 1936, 291, 1341). The dissociation-promoting effect of the phenanthrene nucleus has been studied by determining the dissociation of *s*-diphenanthryltetra-arylethanes (I). Equilibrium solutions of (I) and the corresponding phenanthryldiaryl radicals (II) are prepared by shaking the appropriate phenanthryldiarylchloromethane in C_6H_6 or PhNO_2 with Ag in N_2 . The radicals rapidly absorb O_2 to form the corresponding peroxides. Solutions of 1- (III), 2- (IV), and 3- (V) -phenanthryldiphenylmethyl are relatively stable in the dark, whereas those of 9-phenanthryl-diphenylmethyl (VI) and -diphenylene-methyl (VII) decompose spontaneously. The apparent mol. wts. of the ethanes corresponding with (III), (IV), and (V) and also of *s*-di- α - and β -naphthyl- and *s*-di-*p*-diphenyl-tetraphenylethanes are determined cryoscopically in the filtered solutions. (VI) and (VII) are too unstable to permit mol. wt. determinations. The dissociations calc. from the mol. wts. show that the dissociation-promoting effect of 1- and 2- C_{14}H_9 ranks with that of α - C_{10}H_7 , and is > that of *p*-diphenyl and 3- C_{14}H_9 , while that of the latter two groups is > that of β - C_{10}H_7 .

Benzoylation of phenanthrene gives a mixture of

1- (VIII) and 9-benzoylphenanthrene. (VIII) with MgPhBr gives *diphenyl-1-phenanthrylcarbinol*, m.p. 163—164° [*Me*, m.p. 193—199°, and *Et*, m.p. 151—152°, *ether*; *diphenyl-1-phenanthryl-methane*, m.p. 175—176°, and *-acetic acid*, m.p. 230—232° (decomp.)], which with hot AcCl gives the corresponding *chloromethane* (IX), m.p. 212° (decomp.) (compounds with SnCl_4 , FeCl_3 , and ZnCl_2). On shaking with Ag in C_6H_6 and evaporating, (IX) yields *s-di-1-phenanthryl-tetraphenylethane* as a red oil. *Di(diphenyl-1-phenanthrylmethyl) peroxide* has m.p. 175—176° (decomp.). *Diphenyl-2-phenanthrylcarbinol* [*Me*, m.p. 105—106° and 111—112° (dimorphic), and *Et*, m.p. 116—117°, *ether*; *diphenyl-2-phenanthryl-methane*, m.p. 151—152°, and *-acetic acid*, m.p. 232—233°] from *Me* 2-phenanthroate and MgPhBr , with hot AcCl gives the corresponding *chloromethane*, m.p. 160—161° (compounds with HgCl_2 , SnCl_4 , FeCl_3 , and ZnCl_2), yielding *s-tetraphenyl-di-2-phenanthrylethane* as a red oil. *Diphenyl-3-phenanthrylcarbinol*, m.p. 100—102° (*Me*, m.p. 147—148°, and *Et*, m.p. 155—156°, *ether*; *diphenyl-3-phenanthryl-methane*, m.p. 122—123°, and *-acetic acid*, m.p. 215—216°), is prepared from *Me* 3-phenanthroate and MgPhBr . (The compound previously described as this is the *Me* ether; cf. Bachmann, A., 1935, 622.) Hot AcCl gives the corresponding *chloromethane*, m.p. 132.5—133.5° (compounds with SnCl_4 , FeCl_3 , and ZnCl_2), yielding *s-tetraphenyl-di-3-phenanthrylethane*, m.p. 150—152° (decomp.) in N_2 . *Diphenyl-9-phenanthrylcarbinol* (X) (*Me*, m.p. 165°, and *Et*, m.p. 139—140°, *ether*; *diphenyl-9-phenanthrylacetic acid*, m.p. 257—259° (decomp.)], from $9\text{-C}_{14}\text{H}_9\text{MgBr}$ and COPhMe , gives with hot AcCl 9-phenyl-1:2:3:4-dibenzofluorene (*acetate*, m.p. 254—255°; corresponding *fluorenol*, m.p. 181°; 9-*Cl*-derivative, m.p. 172—174°; *peroxide*, m.p. 209—211°), and with cold AcCl the corresponding *chloromethane* (XI), m.p. 182—183° (decomp.), yielding a very unstable solution of *s-tetraphenyl-di-9-phenanthrylethane*. With Ag in presence of O_2 , (XI) yields *di(diphenyl-9-phenanthrylmethyl) peroxide*, m.p. 184—186° (decomp.), also obtained from (XI) and Na_2O_2 . The spontaneous decomp. of (VI) [also obtained from $9\text{-C}_{14}\text{H}_9\text{CPh}_2\text{Na}$ and $(\text{CMe}_2\text{Br})_2$] gives a *product*, m.p. 275—280° (decomp.) in N_2 , probably a dimeride, analogous to $\text{CHPh}_2\text{C}_6\text{H}_4\text{CPh}_2$ formed from CPh_3 . *Diphenylene-9-phenanthrylcarbinol* (*acetate*, m.p. 113—115°; *Me*, m.p. 231—232°, and *Et*, m.p. 173—174°, *ether*; *diphenylene-9-phenanthryl-methane*, m.p. 192—193°), from $9\text{-C}_{14}\text{H}_9\text{MgBr}$ and *fluorenone*, gives with hot AcCl and AcBr , respectively, the corresponding *chloro-* (XII), m.p. 211—212° (compounds with HgCl_2 and SnCl_4), and *bromo-* (XIII), m.p. 230° (decomp.), *-methanes*. (XII) with Ag in PhBr gives a solution of *s-didiphenylenedi-9-phenanthrylethane*, decomp. on standing. (XIII) with Ag in presence of O_2 gives *di(diphenylene-9-phenanthrylmethyl) peroxide*, m.p. 208—210° (decomp.).

E. G. B.

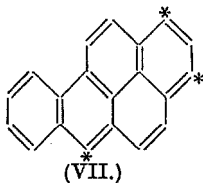
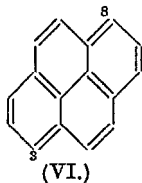
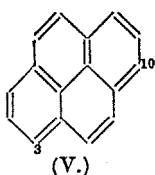
20-tert.-Butylcholanthrene. L. F. FIESER and D. K. SNOW (J. Amer. Chem. Soc., 1938, 60, 176—177).— $p\text{-C}_6\text{H}_4\text{BrBu}^t$, b.p. 228—236°, with $(\text{CH}_2\text{O})_3$, $\text{ZnCl}_2\text{-AlCl}_3$, and HCl at 60—70° give a difficultly separable mixture, b.p. 120—140°/5 mm., of 4-bromo-2- and -3-chloromethyl-tert.-butylbenzene, con-

verted by $\text{CHNa}(\text{CO}_2\text{Et})_2$ into mixed esters, b.p. 190—200°/6 mm., hydrolysis of which affords a mixture, m.p. 132—134°, of β -2-bromo-5- and β -5-bromo-2-tert.-butylphenylpropionic acid. Fractionation of the esters and crystallisation of the acids gave acids, m.p. 151—152° and 138—139°. Pure SOCl_2 and AlCl_3 lead to a mixture, m.p. 69.3—70.3°, of 4-bromo-7- and -7-bromo-4-tert.-butyl-1-hydrindone, reduced by $\text{Zn-Hg-HCl-aq. EtOH}$ to 4-bromo-7-tert.-butylhydrindene, b.p. 149—150°/6 mm. The Grignard reagent therefrom with $\alpha\text{-C}_{10}\text{H}_7\text{CN}$ affords 46% of crude 4- α -naphthoyl-7-tert.-butylhydrindene, pyrolysed at 390—400° in 8% yield to 20-tert.-butylcholanthrene, m.p. 204—205° (corr.) (*picrate*, m.p. 149—150°), which is only slowly, if at all, carcinogenic. 10-Ethyl-1:2-benzanthracene and 20-ethylcholanthrene produce tumours more slowly than do the *Me* homologues.

R. S. C.

1'-Methyl- and 1':10-dimethyl-1:2-benzanthracene. L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1938, 60, 170—176).— $p\text{-C}_6\text{H}_4\text{BrCO}[\text{CH}_2]_2\text{CO}_2\text{H}$ [best (74% yield) prepared from PhBr , $(\text{CH}_2\text{CO})_2\text{O}$, and AlCl_3 at 100°; oxidised to $p\text{-C}_6\text{H}_4\text{BrCO}_2\text{H}$], m.p. 148—149°, is reduced by mossy Zn-Hg in aq. HCl-AcOH-PhMe in 75% yield to γ -*p*-bromophenylbutyric acid, m.p. 71—72°, b.p. 175—176°/3 mm. (with some $\text{Ph}[\text{CH}_2]_3\text{CO}_2\text{H}$), the *chloride*, b.p. 147—148°/4 mm., of which with AlCl_3 in CS_2 gives 7-bromo-1-keto-1:2:3:4-tetrahydronaphthalene, b.p. 142—143°/3 mm., m.p. 76—77°, converted by MgMeCl into 6-bromo-4-methyl-1:2-dihydronaphthalene, b.p. 113—114°/2.5 mm. Dehydrogenation by *S* or *Se* causes loss of *Br*, but addition of *Br* in CCl_4 at -10° and removal of HBr , finally at 200°, gives 59% of nearly pure 7-bromo-1-methylnaphthalene, b.p. 124—125°/3 mm. (*picrate*, m.p. 92.5—93.5°). 1:7- $\text{C}_{10}\text{H}_6\text{MeMgBr}$ and $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ in C_6H_6 give 30% of 7-*o*-carboxybenzoyl-1-methylnaphthalene (I), m.p. (+ Et_2O) 120—126° after softening at 118° and (anhyd.) 153—153.5°, reduced by Zn and aq. NaOH to *o*-8'-methyl-2'-naphthylmethylbenzoic acid (98%), m.p. 143—144°, which with $\text{ZnCl}_2\text{-AcOH-Ac}_2\text{O}$ gives 1-methyl-1:2-benzanthranlyl-9-acetate (II), m.p. 173—174°. $\text{Zn-CuSO}_4\text{-NaOH-H}_2\text{O-PhMe}$ then affords 1'-methyl-1:2-benzanthracene (III), m.p. 138.5—139.2° (*di*-, m.p. 120—121°, and *mono-picrate*, m.p. 129.5—130.5°). Interaction of (II) and MgBu^tBr leads only to 1'-methyl-1:2-benzanthraquinone, m.p. 189—189.5°. With MgMeCl in $\text{Et}_2\text{O-C}_6\text{H}_6$ (I) gives an oily lactone, reduced by Zn-Hg-AcOH-HCl to *o*- α -8'-methyl-2'-naphthylethylbenzoic acid (70%), m.p. 183.5—184.5°, cyclised by ZnCl_2 to 1':10-dimethyl-1:2-benzanthranlyl 9-acetate, m.p. 190—191°, which is reduced by Zn-Hg-NaOH-PhMe to 1':10-dimethyl-1:2-benzanthracene (19%) (IV), m.p. 122.5—123.5° or 124—125° (*picrate*, m.p. 147—148°), with a little of its 9:10- H_2 -derivative, m.p. 113—114° (*picrate*, m.p. 126—127°), also obtained from (IV) by $\text{Na-Et}_2\text{O-C}_6\text{H}_6$. No tumours were obtained by injecting (II) or (IV) into mice, but (IV) causes ulceration. The reactivity of benzpyrene mainly at positions 3 and 10 and to a smaller extent at position 8 indicates the bond structure (V) with a little (VI), whence (VII) becomes probable for 3:4-benzpyrene; reactivity at positions

marked * is then explained, as also is the pharmacological inactivity of (III) and (IV). The stabilising



effect of OH in benzpyrene is discussed. M.p. are corr. R. S. C.

Synthesis and reactions of fluorocyclene. K. DZIEWONSKI and L. GIZLER (Bull. Acad. Polonaise, 1937, A, 441—454).—The best yield of fluorocyclene (*peri*-tetranaphthylencyclooctadiene) (I) (A., 1925, i, 649) is obtained by heating acenaphthene with PbO₂ at 220—280°, or at 180—220° under pressure. At 345—395°/10 mm., (I) decomposes to acenaphthylene, biacene, and decacyclene. With Na in C₅H₁₁OH-xylene, (I) gives *tetrahydro*-, C₄₈H₃₂, m.p. 348—349°, *octahydro*-, m.p. 336—337°, and *doccahydro-fluorocyclene*, m.p. 326°; the structure of these is discussed. E. W. W.

Reduction of aromatic nitro-compounds.

III. Reduction of nitro-compounds and their derived products in presence of acids. V. O. LUKASCHEVITSCH (J. Gen. Chem. Russ., 1937, 7, 2209—2225).— β -Arylhydroxylamines are obtained in 60—70% yield by reducing the corresponding NO₂-compounds with Zn, Cd, or Pb, in AcOH. Reduction with Zn or SnCl₂ in conc. HCl gives anilines, with about 10% of chloroanilines, which are not formed with Fe or Cu. This difference is ascribed to the catalytic action of the systems Fe^{II}-Fe^{III} or Cu^I-Cu^{II} on arylhydroxylamines or arylhydrazines, which are rapidly reduced to amines under the conditions of the experiment, without formation of chloranils, as with Sn, Zn, or Hg. The products of reduction of azobenzenes vary according to the metal and concn. of acid; the velocity of reduction of NO₂-, azoxy-, azo-, aminoazo-, and hydrazo-compounds depends similarly on these and other factors. Hydrazo-compounds are not obligatory intermediates in reduction of NO₂-compounds to amines. R. T.

Reduction of nitro-compounds by iron.—See B., 1938, 136.

Catalytic gas-phase reduction of nitrobenzene to aniline.—See A., I, 150.

Separation of *m*-2-, *m*-4-, and *p*-xylydines.—See B., 1938, 136.

Bromocupric complexes.—See A., I, 91.

Study of the tertiary amine oxide double linking by means of absorption spectra and rotatory dispersion.—See A., I, 64.

Preparation of symmetrical and asymmetric aminopropanediol and their derivatives. H. P. DEN OTTER (Rec. trav. chim., 1938, 57, 13—24).—NH₂CH(CH₂OH)₂ (I) with 1:2:4-C₆H₃Cl(NO₂)₂ in EtOH yields β -(2:4-dinitrophenylamino)propane- α -diol, m.p. 133°, nitrated (fuming HNO₃) to β -(2:4:6-trinitrophenylnitroamino)propane- α -diol dinitrate (II), m.p. 142—143° (decomp.). Similarly are obtained

β -2:4:6-trinitrophenyl-, m.p. 150°, β -2:4-dinitro-naphthyl-, m.p. 199°, and β -5-chloro-2:4-dinitro-phenyl-aminopropane- α -diol (III), m.p. 126—127°, which are nitrated to (II), β -2:4-dinitronaphthyl-, m.p. 117°, and β -3-chloro-2:4:6-trinitrophenyl-nitroaminopropane- α -diol dinitrate, decomp. 40°, respectively. (III) and (I) in EtOH yield 4:6-dinitro-1:3-bis-(β '-dihydroxyisopropylamino)benzene, m.p. 174°, nitrated to 2:4:6-trinitro-1:3-bis-(β '-dihydroxyisopropylnitroamino)benzene tetranitrate, decomp. 50—60°. From α -aminopropane- β -diol (IV) are prepared α -2:4-dinitrophenyl- (V), m.p. 95°, α -2:4:6-trinitrophenyl- (VI), m.p. 136°, α -2:4-dinitronaphthyl- (VII), m.p. 189°, and α -5-chloro-2:4-dinitrophenyl-aminopropane- β -diol (VIII), m.p. 90°. Nitration of (V) and (VI) yields α -2:4:6-trinitrophenyl-, m.p. 80° (decomp.), and of (VII) and (VIII), α -2:4-dinitronaphthyl-, m.p. 80° (decomp.), and α -3-chloro-2:4:6-trinitrophenyl-nitroaminopropane- β -diol dinitrate, m.p. about 50°, respectively. (IV) and (VIII) in EtOH yield 4:6-dinitro-1:3-bis-(β -dihydroxypropylamino)benzene, m.p. 163°, nitrated to 2:4:6-trinitro-1:3-bis-(β -dihydroxypropylnitroamino)benzene tetranitrate, m.p. 73° (decomp.). *d*-Glucosamine similarly yields α β γ δ -tetrahydroxy- ϵ -2:4:6-trinitrophenyl-, m.p. 183°, - ϵ -2:4-dinitronaphthyl-, m.p. 218° (decomp.), and - ϵ -5-chloro-2:4-dinitrophenyl-aminoheptaldehyde, m.p. 190°. Methods of prep. of (I) and (IV) are given. E. I.

Nitrosoacylarylamines. I. Decomposition of nitrosoacetanilide in solution. E. C. BUTTERWORTH and D. H. HEY (J.C.S., 1938, 116—119).—Earlier work (A., 1934, 764; 1935, 78, 828; cf. Waters, A., 1937, II, 97) indicates that the decomp. of NAcPh·NO (I) in C₆H₆ (yielding Ph₂ and N₂) and in other solvents is a free-radical reaction, *i.e.*, (I) \rightarrow Ph· + N₂ + OAc· and OAc· \rightarrow Me· + CO₂. The effect of concn. on the decomp. in C₆H₆ has been studied at 20° with 2—20% solutions. With increasing concn. of (I) the yield of N₂ rises but that of Ph₂ falls, owing to the formation of ter- and polyphenyls. Yields of N₂ and Ph₂ are practically independent of the scale of the reaction (*cf. loc. cit.*). The decomp. of 2% solutions of (I) in C₆H₆ at 10°, 20°, 30°, and 40° shows that with rising temp. the rate of evolution of N₂ increases but the yield of N₂ is unaffected. The best yield of Ph₂ is at 20°. The energy of activation of the reaction is about 22,000 g.-cal. Evolution of N₂ at 20° from 2% solutions of (I) in CHCl₃, CCl₄, C₂HCl₃, C₂H₂Cl₄, C₆H₄Cl₂ (technical), tetralin, decalin, Bu₂O, EtOAc, and *o*-C₆H₄Me·NEt₂ varies widely, indicating reactions between solvent and solute. Rates of evolution of N₂ show that the reactions are unimol. The velocity coeff. is not appreciably affected by the nature of the solvent. Reactions in CCl₄ and C₂HCl₃ yield some PhN₂Cl, and in EtOAc, some Me·CHO. E. G. B.

N-Aryl-N'-dialkylaminoalkylcarbamides as local anaesthetics. H. WENKER (J. Amer. Chem. Soc., 1938, 60, 158—159).—The appropriate carbimide and amine yield *N*-phenyl-N'- β -piperidino-, m.p. 149°, and -N'- β -di-n-butylamino- (I), m.p. 113°, *N*-*o*-anisyl-N'- β -piperidino-, m.p. 135°, and -N'- β -di-n-butylamino- (II), m.p. <94°, and *N*-*p*-ethoxy-

phenyl-N'-β-piperidino-isopropylcarbamide, m.p. 124°, and *N-phenyl-N'-β-piperidinoisopropylthiocarbamide*, m.p. 123°. The hydrochlorides of (I) and (II) are local anaesthetics. Piperidine and NH_4Bu^2 with propylene oxide give *N-β-hydroxy-n-propylpiperidine* and *β-hydroxy-n-propyldibutylamine*, b.p. 130°/15 mm., converted by SOCl_2 into the *hydrochlorides*, m.p. 204° and an oil, respectively, of *N-β-chloro-n-propylpiperidine* and *β-chloro-n-propyldibutylamine*, which with $\text{NH}_3\text{-MeOH}$ at 60° give *N-β-amino-n-propylpiperidine*, b.p. 193—194°, and *β-amino-n-propyldibutylamine*, b.p. 132°/15 mm. R. S. C.

Anthranyl- and 1:2:5:6-dibenzanthranyl-carbimides. I. H. J. CREECH and W. R. FRANKS (J. Amer. Chem. Soc., 1938, 60, 127—128).—By the use of a large excess of COCl_2 , 9-aminoanthracene, if rigidly purified, gives 80% of 9-anthranylcarbimide, m.p. 75.5—76.5°, which affords *Me*, m.p. 265—266°, and *Et* 9-anthranylcarbamate, m.p. 236.5—237°, and β-9-anthranylcarbamidoethyl alcohol, m.p. 263—264°. 1:2:5:6-Dibenzanthranylcarbimide (prep. in 75% yield), m.p. 181—181.5°, gives *Me*, m.p. 264—265°, and *Et* 1:2:5:6-dibenzanthranyl-9-carbamate, m.p. 224—224.5°, and β-1:2:5:6-dibenzanthranyl-9-carbamidoethyl alcohol, m.p. 308—309°. Carbamides are obtained, but are difficult to purify. Experiments are usually carried out in N_2 . R. S. C.

Reaction of dienes with diazo-compounds. B. ARBUSOV and S. RAFIKOV (J. Gen. Chem. Russ., 1937, 7, 2195—2201).— $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ in aq. HCl and $(\text{CH}_2\cdot\text{CH})_2$ at 0° yield $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ and α-(*p*-nitrobenzeneazo)butadiene, m.p. 118—119°, converted by reduction (SnCl_2 in HCl) into $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and pyrroline. The product obtained similarly with $(\text{CHMe}\cdot\text{CH})_2$ is β-(*p*-nitrobenzeneazo)-Δ⁸-hexadiene, m.p. 172—173°, reduced to 2:5-dimethylpyrroline. R. T.

Azo-dyes and their intermediate products. XIX. Tolane and deoxybenzoin dyes. P. RUGGLI and F. LANG (Helv. Chem. Acta, 1938, 21, 38—50; cf. A., 1936, 1373).—Chlorination of 4:4'-dinitrostilbene (I) in strongly illuminated, boiling AcOH gives a mixture of products from which 4:4'-dinitrotolane (II) is obtained in reasonable yield. Better results are obtained in hot PhNO_2 , whereby the dichloride, m.p. 282—286°, is readily isolated. The best process consists in adding Br in PhNO_2 to (I) in hot PhNO_2 and conversion of the dibromide, m.p. 283°, into (II) by KOH-MeOH . Hydrogenation ($\equiv 12\text{ H}$; Ni in $\text{EtOAc-EtOH-H}_2\text{O}$) of homogeneous (II) gives 4:4'-diaminotolane (III) in good yield accompanied by a small proportion of *cis*-4:4'-diaminostilbene. (III) gives *Ac*₂, m.p. 281°, *Bz*₂, m.p. 332°, and $(\text{CHPh})_2$, m.p. 207°, derivatives. Diazotisation of (III) followed by coupling with 2 mols. of naphthionic acid gives *tolane-red* (IV), $[\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{NH}_2)\cdot\text{SO}_3\text{Na}]_2$, whilst with 1:4- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ *tolane-violet*, $[\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{Na}]_2$, is produced. Both are substantive dyes to cotton, which is dyed by the latter only in presence of Na_2SO_4 . Both are colloidal. Attempts to establish the constitution of (IV) by reductive fission were unsuccessful since from the strongly acid solution (V) (below) is isolated. The

acetylenic linking persists after tetrazotisation since treatment of the solution with EtOH leads to tolane free from CH_2PhBz . Treatment of (III) with dil. HCl at 100° and then at the b.p. of the solution gives 4:4'-diaminodeoxybenzoin (V), m.p. 145° [*oxime*, m.p. 146°; $(\text{CHPh})_2$ derivative, m.p. 181°], in 50% yield. Treatment of (V) with 2 mols. of HNO_2 and of the product with naphthionic acid gives the red dye, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{NH}_2)\cdot\text{SO}_3\text{Na}$, in which free NH_2 can be detected by after-diazotisation on the fibre and development with H -acid or, preparatively, by diazotisation and coupling with 6:2- $\text{C}_{10}\text{H}_6\cdot\text{Br}\cdot\text{OH}$. Condensation of $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ in presence of piperidine gives essentially *trans*-4:4'-dinitrostilbene-7-carboxylic acid (cf. Cullinane, A., 1923, i, 606). $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$, Ac_2O , and ZnCl_2 give *cis*-4:4'-dinitrostilbene-7-carboxylic acid, m.p. 265—267°, decarboxylated by Cu powder in quinoline at 210° to *cis*-4:4'-dinitrostilbene, m.p. 185—186°, isomerised by I in PhNO_2 at 210° to the corresponding *trans*-compound, m.p. 286—287°, and reduced (Ni in $\text{EtOAc-EtOH-H}_2\text{O}$) to the *cis*-4:4'-(NH_2)₂-compound. H. W.

Union of aryl nuclei. I. Extensions of the Gomberg reaction. W. S. M. GRIEVE and D. H. HEY [with, in part, J. L. DUNN and E. R. B. JACKSON] (J.C.S., 1938, 108—113).—Methods of synthesis of unsymmetrical diaryls from diazo-compounds are reviewed. Attempts have been made to increase the yield from the normal Gomberg reaction (cf. A., 1924, i, 1295; 1926, 944) using PhN_2Cl and C_6H_6 , the NaOH being (i) added to the mixture of PhN_2Cl and C_6H_6 , or (ii) mixed with C_6H_6 and the PhN_2Cl added to the mixture. Method (i) has been used in presence of MgSO_4 (cf. Gomberg and Bachmann, A., 1927, 245), CuSO_4 , and CH_2O , with aq. NH_3 and NaOAc in place of NaOH , and in N_2 . Method (ii) has been used with addition of lissapol A, with $\text{Ca}(\text{OH})_2$ for NaOH , and at 30° and 50°. In no case was the yield of Ph_2 markedly affected. No diaryl is formed from PhN_2Cl or *o*- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ (I) and aq. NaOBz , or from (I) and C_6H_6 , whereas reaction of MeOBz with PhN_2Cl (cf. *idem*, A., 1924, i, 1295) or of *o*- $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ (II) with C_6H_6 is normal. These results indicate that two phases are essential and that reaction takes place in the non-aq. medium and is probably non-ionic. The use of solid reactants (in solution) in the Gomberg reaction requires the solvent to be neutral, H_2O -immiscible, and inert towards diazo-compounds. CHCl_3 and CCl_4 give low yields of diaryl, some reaction with the solvent occurring; thus PhN_2Cl with CCl_4 gives some PhCl . This is in accord with the view (cf. A., 1935, 78; 1934, 764; Waters, A., 1937, II, 97) that these reactions involve formation of free radicals, which react also with the solvent. (II) with C_{10}H_8 in CCl_4 , PhN_2Cl with Ph_2 in CHCl_3 or CCl_4 , $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ with Ph_2 in CHCl_3 , and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ with COPh_2 in CCl_4 , give respectively *Me o-α-naphthylbenzoate*, m.p. 87—88° (the free acid gives *ms*-benzanthrone on ring-closure), *p*- $\text{C}_6\text{H}_4\text{Ph}_2$, 4'-nitro-*p*-diphenylbenzene, and 4-methoxy-4'-ben-

zoilydiphenyl (also obtained from BzCl , 4-methoxydiphenyl, and AlCl_3). Diazotised α - and β - $\text{C}_{10}\text{H}_7\text{NH}_2$ with C_6H_6 give respectively 1- and 2- $\text{C}_{10}\text{H}_7\text{Ph}$ in small yield. E. G. B.

Introduction of deuterium into the aromatic nucleus. II. Orientation of certain substituents. A. P. BEST and C. L. WILSON (J.C.S., 1938, 28—29).—Bromination of deuterated PhOH and NH_2Ph gives the corresponding 2:4:6- Br_3 -derivatives, free from D, showing that the deuteration had been exclusively *ortho-para*, in agreement with the hypothesis that nuclear deuteration in aromatic compounds is an electrophilic substitution (cf. A., 1936, 1322). E. G. B.

Thermal and catalytic decomposition of phenoxides. VIII. Influence of the methoxy-group. Preparation and properties of the sodium, potassium, and silver salts of halogenated *p*-methoxyphenols. IX. Influence of the *o*-methoxy-group. X. Influence of the methyl group. Preparation and properties of the sodium and potassium salts of *o*- and *p*-cresols. XI. Preparation and properties of silver phenoxides. W. H. HUNTER and F. F. RATMAN (J. Gen. Chem. Russ., 1937, 7, 2202—2205, 2206—2208, 2226—2229, 2230—2234).—VIII. Attempted iodination in aq. KOH of $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ (I) led to the production of amorphous polymerisation products only. (I) and Br in AcOH give 2:5-dibromo-4-methoxyphenol, the Na salt of which is highly unstable, and could not be obtained pure. Bromination in absence of AcOH gives 2:3:5:6-tetrabromo-4-methoxyphenol (K, +1, 2, and $3\text{H}_2\text{O}$, Na, and Ag salts). The OMe in *p*-position confers instability, and Br *meta* to OH stability, to the salts.

IX. The Ag salts of trichloro- or tribromo-pyrogallol Me_2 ether are decomposed by hot H_2O with liberation of Ag. In boiling C_6H_6 the products are AgCl(Br) and amorphous polymerides, $\approx 5\%$ of the OMe being eliminated during the process. Introduction of OMe *ortho* to OH does not affect the process of polymeride formation, but favours decomp. of Ag salts with liberation of Ag.

X. The Na and K salts of 3:5-di-iodo- and -bromo-*o*- and -*p*-cresol are described, and their relative stability under the above conditions is determined.

XI. The Ag salts of 3:5-di-iodo- and -bromo-*o*- and -*p*-cresol are described, and evidence is adduced that the coloured forms of such salts possess a quinonoid structure; the intensity of the coloration and the stability of the salts fall in the order $\text{I} > \text{Br} > \text{Cl}$ for mono-, di-, and tetra- and in the reverse order for tri-halogen derivatives. R. T.

Nitration of acyl derivatives of 4:5-dibromo- and 4:5:6-tribromo-guaiacol. L. C. RAIFORD and R. E. SILKER (J. Org. Chem., 1937, 2, 346—355).—4:5-Dibromo- (I) and 4:5:6-tribromo- (II) -guaiacol cannot be nitrated by HNO_2 or fuming HNO_3 , although a reaction occurs in the latter case, probably complete oxidation. The Ac derivative, m.p. 101—102°, of (I) gives with fuming HNO_3 4-bromo-5-nitro-2-methoxy- (III), m.p. 160—161°, and 4:5-dibromo-3-nitro-2-methoxy- (IV), m.p. 91.5—92.5°, -phenyl acetate. (III) is hydrolysed to 4-bromo-5-

nitroguaiacol (V), m.p. 118—119°, this structure being preferred to the alternative 5:4-structure since OMe has greater *o-p*-directing influence than OAc. Meldola and Streatfield's bromonitroguaiacol (J.C.S. 1898, 73, 689) is probably (V), which is methylated to 4-bromo-5-nitroveratrol. The structure of (IV) is shown by its hydrolysis to 4:5-dibromo-3-nitroguaiacol (VI), m.p. 164—165°, which is methylated to 4:5-dibromo-3-nitroveratrol. The Bz derivative, m.p. 110.5—111.5°, of (I) with fuming HNO_3 yields only 4:5-dibromo-3-nitro-2-methoxyphenyl benzoate, m.p. 116—117°, giving (VI) on hydrolysis. Similarly the Ac, m.p. 119—120°, and Bz, m.p. 148—149°, derivatives of (II) give with fuming HNO_3 4:5:6-tribromo-3-nitro-2-methoxyphenyl acetate (VII), m.p. 98—99°, and benzoate (VIII), m.p. 140—141° [together with 3—4% of the *m*-nitrobenzoate (IX), m.p. 202—203°], respectively. On hydrolysis (VII), (VIII), and (IX) all give 4:5:6-tribromo-3-nitroguaiacol, m.p. 101—102° (O- CO_2Me , m.p. 105—108°, and O- CO_2Et , m.p. 93—94°, derivatives). These results support the view that acylation of a OH in a C_6H_6 derivative suppresses its directive influence. 4:5:6-Tribromo-3-nitroveratrole has m.p. (new) 122—123°. E. G. B.

Complex compounds of picric acid and other nitrophenols with cuprammonium salts. N. P. AGAFOSCHIN (J. Gen. Chem. Russ., 1937, 7, 2235—2239).—The compounds

$[\text{2:4:6-(NO}_2)_3\text{C}_6\text{H}_2\text{O}]_2\text{Cu(NH}_3)_4$ and $[\text{2:4-(NO}_2)_2\text{C}_6\text{H}_3\text{O}]_2\text{Cu(NH}_3)_4$ are obtained by adding aq. picric acid or 2:4-(NO_2) $_2\text{C}_6\text{H}_3\text{OH}$, respectively to aq. cuprammonium hydroxide. Pure products were not obtained analogously with *o*-nitro-phenol or -cresol. R. T.

Polyalkylphenols.—See B., 1938, 139.

Condensation of tertiary aryl-substituted carbinols with phenol in the presence of aluminium chloride. L. H. WELSH [with N. L. DRAKE] (J. Amer. Chem. Soc., 1938, 60, 59—62).—In presence of AlCl_3 $\text{CPhMe}_2\cdot\text{OH}$ and PhOH give 68—72% of *p*- α -phenylisopropylphenol (I), b.p. 213—214°/25 mm., m.p. 73° (corr.) (diphenylurethane, m.p. 126°; gives *p*- α -phenylisopropylphenoxyacetic acid, m.p. 117°), and some 3-phenyl-1:1:3-trimethylhydrindene (formed by polymerisation of $\text{CPhMe}\cdot\text{CH}_2$). The structure of (I) is proved by its methylation to, and prep. by HBr from, *p*- α -phenylisopropylanisole, b.p. 198—199°/25 mm., which is obtained from $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$ and CPhMe_2Cl . $\text{CPh}_2\text{Me}\cdot\text{OH}$ gives 80% of *p*- $\text{CPh}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ with $\text{CPh}_2\cdot\text{CH}_2$ and a resinous (?) polymeride. $\text{CPh}_3\cdot\text{OH}$ gives 95% of *p*- $\text{CPh}_3\cdot\text{C}_6\text{H}_4\cdot\text{OH}$. Dehydration of the carbinols, when possible, to the ethylene is indicated by the isolation of the ethylenes or their polymerisation products, and by the fact that $\text{CH}_2\text{Ph}\cdot\text{CPh}_2\cdot\text{OH}$ and C_6H_6 give $(\text{CHPh})_2$ and not $\text{CH}_2\text{Ph}\cdot\text{CPh}_3$. R. S. C.

N-Aralkylaminophenols.—See B., 1938, 139.

Electrolytic substitution in naphthols. II. Electrolytic introduction of the nitroso-group into naphtholsulphonic acids. K. EMI (Rep. Imp. Ind. Res. Inst., Osaka, 1935, 16, No. 9, 1—28; cf. B., 1935, 1036).—The yield of nitroso-

naphtholsulphonic acid is $>$ that of $\text{NO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$. $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_2$ gives a better yield than $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{H}$. Introduction of SO_3H increases the yield of the NO-compound. When 1:4- $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{H}$ is electrolysed in aq. $\text{NaOAc} - \text{NaNO}_2$, 1:2:4- $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{NO}_2)_2$ is produced in addition to the NO-compound. CH. ABS. (e)

Isomerisation during Grignard synthesis. Isomeride of amber musk. B. M. DUBININ (J. Gen. Chem. Russ., 1937, 7, 2183—2187).—5-Bromo-3-methoxytoluene, Mg, and Bu^tI in Et_2O do not react until most of the Et_2O has distilled off; the residue is heated under reflux for 30 min., when 3-methoxy-4-*tert.*-butyltoluene (I) is obtained in 40% yield. The product obtained by using MeI in place of Bu^tI is 5-methoxy-*m*-xylene. Migration of the Bu^t group is ascribed to formation of CMe_2CH_2 , which condenses with 3-methoxytoluene to yield (I). R. T.

Synthesis of mono-ethers of 2:4-di(hydroxymethyl)anisole. M. ANGLADE (Compt. rend., 1937, 205, 1158—1160; cf. A., 1936, 1247).—2:4-Di(methoxymethyl)anisole with $\text{AcCl} - \text{ZnCl}_2$ in light petroleum (cf. A., 1933, 710) gives 4-chloromethyl-2-methoxymethylanisole (I), which with $\text{AcOH} - \text{NaOAc}$ followed by aq. $\text{EtOH} - \text{KOH}$ at room temp. affords 4-hydroxymethyl-2-methoxymethylanisole, b.p. $141^\circ/5$ mm. (phenylcarbamate, m.p. 73.5°). The *OEt*-analogue has b.p. $142^\circ/4$ mm. (phenylcarbamate, m.p. 58.5°). (I) and its *OEt*-analogue with $(\text{CH}_2)_6\text{N}_4$ afford 4-methoxy-3-methoxymethyl- and -3-ethoxymethylbenzaldehyde (cf. A., 1937, II, 422), respectively, thus proving the structures of the OH-derivatives. J. L. D.

Pyrolysis of alkylallyl and alkylcrotyl ethers of phenol and *o*-cresol. C. D. HURD and M. P. PUTERBAUGH (J. Org. Chem., 1937, 2, 381—386).—Pyrolysis of ethers $\text{OPh} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CHR}$ ($\text{R} = \text{Et}$, Pr , or Bu) gives mixtures of *o*-alkenylphenols, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHR} \cdot \text{CH} \cdot \text{CH}_2$, and $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHR}' \cdot \text{CH} \cdot \text{CHR}''$ (cf. Lauer and Filbert, A., 1936, 1244). Small amounts of PhOH are also formed. The corresponding *o*-tolyl ethers similarly give 6-alkenyl-2-methylphenols and *o*-cresol. Phenyl and *o*-tolyl α -alkylcrotyl ethers on pyrolysis give mainly alkali-insol. products; PhOH and *o*-cresol are also formed. The following are described. Δ^8 -Octen-8-ol, b.p. $74^\circ/8$ mm. (from $\text{CHMe} \cdot \text{CH} \cdot \text{CHO}$ and MgBu^tBr); δ -chloro- Δ^8 -octene, b.p. $69-70^\circ/9$ mm.; *o*-pentenyl-, b.p. $110-112^\circ/7$ mm., *o*-hexenyl-, b.p. $120-122^\circ/6-7$ mm., *o*-heptenyl-, b.p. $125-127^\circ/6$ mm., 6-pentenyl-2-methyl-, b.p. $107-110^\circ/3$ mm., 6-hexenyl-2-methyl-, b.p. $112-115^\circ/3$ mm., and 6-heptenyl-2-methyl-, b.p. $120-121^\circ/4$ mm., -phenol; *Ph* γ -ethyl-, b.p. $91-95^\circ/4$ mm., γ -*n*-propyl-, b.p. $105-107^\circ/4$ mm., and γ -*n*-butyl-, b.p. $102-103^\circ/3$ mm., -allyl ethers; *Ph* α -ethyl-, b.p. $89-91^\circ/5$ mm., α -*n*-propyl-, b.p. $103-104^\circ/4$ mm., and α -*n*-butyl-, b.p. $107-108^\circ/4$ mm., -crotyl ethers; *o*-tolyl γ -ethyl-, b.p. $106-108^\circ/3$ mm., γ -*n*-propyl-, b.p. $115-117^\circ/6$ mm., and γ -*n*-butyl-, b.p. $105-108^\circ/3$ mm., -allyl ethers; *o*-tolyl α -ethyl-, b.p. $100-102^\circ/6$ mm., α -*n*-propyl-, b.p. $96-98^\circ/4$ mm., and α -*n*-butyl-, b.p. $118-119^\circ/4$ mm., -crotyl ethers.

The following new physical data, *inter alia*, are

recorded: pyrocatechol monoallyl, b.p. $103-104.5^\circ/8$ mm., and diallyl, b.p. $112-115^\circ/8$ mm., ether; 3-, b.p. $132-138^\circ/9$ mm., and 4-allyl-, b.p. $141-144^\circ/7$ mm., 3:6-di-, b.p. $132-137^\circ/6$ mm., and tri-, b.p. $175-180^\circ/10$ mm., -allyl-pyrocatechol; allylpyrocatechol diallyl, b.p. $140-155^\circ/12$ mm., and resorcinol monoallyl, b.p. $130-135^\circ/7$ mm., ether; 4-mono-, b.p. $143-150^\circ/5-9$ mm.; and 4:6-di-, b.p. $178-183^\circ/12$ mm., -allylresorcinol. E. G. B.

Cleavage of diphenyl ethers by sodium in liquid ammonia. III. 4:4'-Disubstituted diphenyl ethers. F. C. WEBER and F. J. SOWA (J. Amer. Chem. Soc., 1938, 60, 94—95; cf. A., 1937, II, 412).—By cleavage of $\text{C}_6\text{H}_4\text{R} \cdot \text{O} \cdot \text{C}_6\text{H}_4\text{R}'$ by Na the following effectiveness of *p*-substituents in strengthening the O-Ar linking is demonstrated: $\text{Me} < \text{Bu}^t < \text{OMe} < \text{NH}_2$. This order is also that of increasing *o*-*p*-directing power. The following order of electro-negativity of substituted Ph is deduced: $p > o > m$ - $\text{NH}_2 > p$ - $\text{OMe} > p$ - $\text{Bu}^t > p > m > o$ - $\text{Me} > \text{H} > m > o$ - $\text{OMe} > m > o > p$ - CO_2H . *p*-Anisyl *p*-tolyl, m.p. $49-50^\circ$, b.p. $193-198^\circ/22$ mm., and *p*-hydroxyphenyl ether, m.p. $64-65^\circ$, b.p. $183-193^\circ/16$ mm., and *p*-tolyl *p*-*tert.*-butylphenyl ether, b.p. $174-178^\circ/4$ mm., are prepared. R. S. C.

Action of nitrous acid on (phenyl-2-hydroxy- α -naphthylmethyl)amine. III. F. E. RAY and W. R. HAEFELE (J. Amer. Chem. Soc., 1938, 60, 36—38; cf. A., 1935, 97).— $\frac{1}{2} > \text{C}_{10}\text{H}_6 < \begin{matrix} \text{CHPh} \\ \text{O} \cdot \text{CHPh} \end{matrix} > \text{NH}$ (I) and $\text{Na} - \text{Hg} - \text{CO}_2$ in EtOH at 60° give *N*-benzyl-*N*-(phenyl-2-hydroxy- α -naphthylmethyl)amine, m.p. 143° (hydrochloride, m.p. 176° ; violet FeCl_3 colour). Similar reduction of the NO-derivative of (I) gives (?) the substance $\text{CH} < \begin{matrix} \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CHPh} \\ \text{CH} - \text{CH} - \text{O} \end{matrix} > \text{C}_{10}\text{H}_6 < \frac{1}{2}$, m.p. 141° (no FeCl_3 colour; stable to HCl), probably by partial reduction to $\text{CH}_2\text{Ph} \cdot \text{NH} \cdot \text{NH}_2$, partial hydrolysis to β - $\text{C}_{10}\text{H}_7 \cdot \text{OH}$, and union of the products. Passage of N_2O_3 into 2:1- $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CHPh} \cdot \text{NH}_2$ (II) in $\text{Et}_2\text{O} - \text{Ac}_2\text{O} - \text{AcOH}$ gives a substance, $\text{C}_{21}\text{H}_{20}\text{O}_2\text{N}_2$, m.p. 125° [Liebermann reaction positive; no FeCl_3 colour; regenerates (II) with HCl ; gives the CHI_3 and cacodyl oxide reactions], reduced by $\text{Na} - \text{Hg}$ to a substance, $\text{C}_{24}\text{H}_{33}\text{O}_2\text{N}$, m.p. 137° [blue FeCl_3 colour; with HCl gives PhCHO and (II)]. R. S. C.

Hydroxydiphenyl sulphides.—See B., 1938, 139.

Quinol and its oxidation products in alkaline solutions. H. STAUDE (Z. wiss. Phot., 1938, 37, 3—5).—Quinol solutions free from *p*-benzoquinone (I) can be prepared by steam-distillation at low pressure in pure N_2 , crystallising the quinol, and dissolving it in alkali carbonate solution, all in an O_2 -free atm.; a simpler method is to reduce any (I) by treating the solution (in O_2 -free atm.) with Gladstone-Tribe $\text{Cu} - \text{Zn}$ couple, and then add the solution to the alkali carbonate solution, also under N_2 . Pure quinol is colourless. Absorption curves are given. The solutions keep indefinitely under N_2 , but discolour rapidly in air. If little alkali is present, the (I) can be extracted with Et_2O , but not if more alkali is added. (I) (without air, *e.g.*, under PhMe) gives with NaOH a blue-green colour (hydroxy-

quinonate) which turns red with acid (hydroxyquinone), the reaction being reversible and the inversion point p_H 9.5. Other reactions are given. J. L.

Oxidation processes. XI. Autoxidation of duroquinol. T. H. JAMES and A. WEISSBERGER (J. Amer. Chem. Soc., 1938, **60**, 98—104; cf. A., 1937, I, 623).—Duroquinol (I) in alkali is oxidised quantitatively to duroquinone (II) and H_2O_2 . The rate is dependent on $[OH^-]^2$, showing that the first step is formation of $O^{\cdot-} \cdot C_6Me_4 \cdot O^{\cdot-}$. Two processes then occur, viz., (a) reaction of the ion with O_2 , the rate being $\propto [O_2]$ and the concn. of (I), and (b) further reaction with (II) (if present), the rate being \propto the concn. of (I) and (II) and independent of the $[O_2]$. The autoxidation is catalysed by $CuSO_4$, the rate of this reaction being $\propto [O_2]$. Na_2SO_3 is not an inhibitor. At high alkalinity relatively slow autoxidation of (II) occurs. R. S. C.

Additive compounds of dihydric phenols. Y. GARREAU (Compt. rend., 1937, **205**, 1072—1074).—Addition of quinol to a solution of $(CH_2 \cdot NH_2)_2$, SO_2 , and the metallic hydroxide gives compounds $3C_6H_4(OH)_2 \cdot 2(CH_2 \cdot NH_2)_2 \cdot X \cdot 2H_2O$ in which $X = Cu, Zn$, and Cd and the substance $6C_6H_4(OH)_2 \cdot 7(CH_2 \cdot NH_2)_2 \cdot 4NiSO_3 \cdot 8H_2O$. Under analogous conditions resorcinol gives only the compound $C_6H_4(OH)_2 \cdot 2(CH_2 \cdot NH_2)_2 \cdot CuSO_3 \cdot H_2O$. H. W.

Antiseptics. IV. Alkylpyrocatechols. E. MILLER, W. H. HARTUNG, H. J. ROCK, and F. S. CROSSLEY (J. Amer. Chem. Soc., 1938, **60**, 7—10; cf. A., 1933, 499).—Conditions are given for the prep. of o - $C_6H_4(O \cdot CO \cdot Alk)_2$ and their rearrangement by $AlCl_3$ in presence of o - $C_6H_4(OH)_2$ in CS_2 in good yield to 4-acylpyrocatechols with smaller amounts of the 3-isomerides. Isolation of the acyl chloride or the ester is unnecessary. The same products are obtained from acylguaiacols. Thus are prepared 4-*n*-butyryl-, m.p. 139°, 4-*n*-, m.p. (anhyd.) 93—94° (lit. 143—144°) or (+0.5 H_2O or 0.5 dioxan) 100—101°, 4-*iso*-, m.p. 106.5—107.5°, and 3-*iso*-valeryl-, m.p. 93—95°, 4-*n*-, m.p. 93.8° [some 4:3:1- $OH \cdot C_6H_3(OMe) \cdot CO \cdot C_5H_{11}$ is also obtained from guaiacol], 4-*iso*-, m.p. 73—73.5°, and 3-*iso*-hexoyl-, b.p. 195—205°/(? 4 mm.), 4-*n*-heptyl-, m.p. 78—79°, 4-, m.p. 95.5—96°, b.p. 225°/5 mm., and 3-*n*-octoyl-, m.p. 87—88°, and 3-*propionyl*-pyrocatechol, b.p. 182—187°/5 mm., m.p. 102.5—103.5°. Reduction by H_2 -Pd or, less well, by Zn - Hg - HCl gives 4-*n*-butyl-, (I), b.p. 143—147°/5 mm., 4-*n*-, b.p. 158—159°/7 mm., and -*iso*-amyl-, b.p. 155—160°/6 mm., m.p. 55.5—58.5°, 4-*n*- (II), b.p. 164—169°/5 mm., and -*iso*-hexyl-, b.p. 161—164°/5 mm., 4-*n*-heptyl- (III), b.p. 195—200°/12 mm., m.p. 40°, and 4-*n*-octyl-pyrocatechol, b.p. 178°/5 mm., m.p. 40°. $PhOH$ coeffs. against *S. aureus* are (I) 29, (II) 129, and (III) 177, showing the effect of alkyl. R. S. C.

Organic reactions with boron fluoride. XVII. J. F. McKENNA and F. J. SOWA (J. Amer. Chem. Soc., 1938, **60**, 124—125).—Fluorescein is prepared in almost quant. yield by use of BF_3 in C_6H_6 , and phenolphthalein in 72% yield by BF_3 without solvent. Nitriles and alcohols react thus: $3ROH + R'CN + BF_3 \rightarrow BF_3 \cdot NH_3 + CR'(OR)_3 \rightarrow R'CO_2R +$

R_2O , yields being moderate; this mechanism is confirmed by decomp. of $CH(OEt)_3$ into $HCO_2Et \cdot BF_3$ and $Et_2O \cdot BF_3$. In presence of BF_3 , esters and NH_2Ph give anilides (2—10%) and alcohols. Bu^tOH and Bu^iOH with $PhOH$ and BF_3 give p - $C_6H_4Bu^t \cdot OH$ as main product. R. S. C.

Preparation of glycerides of phenyl-substituted aliphatic acids and their reduction to alcohols. Preparation of phenylethyl alcohol. G. DARZENS (Compt. rend., 1937, **205**, 682—684).—Glycerides of $CH_2Ph \cdot CO_2H$ (I) are prepared in good yields from (I), glycerol (II), and HCl first at 145—150°, and subsequently at 135—140°/15 mm. for 16—20 hr. Excess of (II) gives the α -monoglyceride, and excess of (I) the triglyceride, neither obtained cryst. (II) (1 mol.) with 2 mols. of (I) yields the α -diglyceride, m.p. 62.5°, of (I). On reduction (Na , amyl alcohol) the glycerides all give $Ph \cdot [CH_2]_2 \cdot OH$ [prep. from (I) and (II) described]. Homologues of (I) behave similarly; $Ph \cdot [CH_2]_2 \cdot CO_2H$ gives the triglyceride, reduced to $Ph \cdot [CH_2]_3 \cdot OH$, also obtained by reduction of the triglyceride, m.p. 111°, of cinnamic acid.

E. G. B.

Catalytic hydrogenation of β -ionone: dihydro- β -ionone, dihydro- β -ionol, and derivatives of α - and β -ionol. J. KANDEL (Compt. rend., 1937, **205**, 994—996).— β -Ionone (I) is hydrogenated (H_2 - Ni) at 150 kg. per sq. cm. at room temp. to dihydro- β -ionone (II); at 90°, a mixture of (II) and dihydro- β -ionol, b.p. 132.5°/14 mm., m.p. 39.5° (allopphanate, m.p. 171.5°), is formed. Reduction of (I) with $Al(OPr^i)_3$ yields β -ionol (III), b.p. 130.5°/14.5 mm., whilst dehydration of α -ionol and (III) (SiO_2 gel at 300°) yields respectively 3- β 88-, b.p. 96—97°/16.5 mm., and 2- α - γ -trimethylbutadienylcyclohexene, b.p. 108—110°/15 mm. The *Me*, b.p. 115°/15.5 mm., and *Et* ethers, b.p. 120°/14 mm., *formate*, b.p. 127.5—128°/15 mm., *acetate*, b.p. 134°/15 mm., *propionate*, b.p. 144—145°/15 mm., *benzoate*, b.p. 168—169°/2 mm., *p*-nitrobenzoate, m.p. 88°, and *allopphanate*, m.p. 151—152°, of α -ionol and the *acetate*, b.p. 136.5°/14.5 mm., *propionate*, b.p. 145—146°/15 mm., *isobutyrate*, b.p. 150°/15.5 mm., *benzoate*, b.p. 205—206°/15 mm., and *p*-nitrobenzoate, m.p. 85°, of (III) are described.

J. D. R.

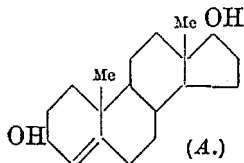
Menthadiene hydrocarbons obtained by dehydration of active and inactive 3-methyl-1-(α -hydroxyisopropyl)cyclohexanols. M. GODCHOT and (MLLE.) G. CAUQUIL (Compt. rend., 1938, **206**, 88—90; cf. A., 1937, II, 241).—*Me* 1-3-methylcyclohexanol-1-carboxylate (cf. *ibid.*, 62) with $MgMeI$ affords 1-3-methyl-1-(α -hydroxyisopropyl)cyclohexanol (I), m.p. 52°. *Me* dl-3-methylcyclohexanol-1-carboxylate, b.p. 109—110°/15 mm., similarly affords dl-3-methyl-1-(α -hydroxyisopropyl)cyclohexanol (II), m.p. 47°. (I) and (II) with aq. $H_2C_2O_4$ at 120° afford 1-, $[\alpha]_{5780} -103.5^\circ$, and dl-1-methyl-3-isopropenyl- $\Delta^{2 \text{ or } 3}$ -cyclohexene, b.p. 184°/745 mm., respectively (together with ketonic material), which with H_2 -Raney Ni give d-, b.p. 165°/760 mm., $[\alpha]_{5780} +22.48^\circ$, and dl-1-methyl-3-isopropyl- $\Delta^{2 \text{ or } 3}$ -cyclohexene, b.p. 165°/760 mm., respectively. These are reduced (H_2 - PtO_2) to 1-, b.p. 167°/760 mm., $[\alpha]_{5780} -1.36^\circ$, and dl-1-methyl-3-isopropylcyclohexane, b.p. 167°/760

mm., respectively. The Raman spectra of the hydrocarbons are determined. J. L. D.

Dehalogenation by silver [nitrate] of the iodo-hydrins of α -cyclanediols. M. TIFFENEAU and B. TCHOUBAR (Compt. rend., 1937, 205, 1411—1413).—Dehalogenation of 2-iodo-1-methylcyclohexanol with AgNO_3 (cf. A., 1933, 384) gives 2-methylcyclohexanone (I) with 10% of acetylcyclopentane (II); (I) is a secondary product formed by the action of nitric acid on the primary epoxide (III). Dehalogenation with Ag_2O gives (III) (80%), the corresponding glycol (IV) (10%), (II) (5%), and some (I) possibly arising from a small trace of *cis*-iodohydrin. The action of cold HNO_3 on (III) causes immediate isomerisation into (I) and hydration to (IV) without production of (II). 2-Iodo-1-ethylcyclohexanol, obtained by the action of HOI on Δ^1 -ethylcyclohexene, is transformed by AgNO_3 mainly into the nitrate of the corresponding glycol and into the epoxide (V), which is isomerised by the liberated HNO_3 to 2-ethylcyclohexanone (VI) and hydrated to *trans*-2-ethylcyclohexane-1:2-diol (VII). Propionylcyclopentane is also formed in small proportion. This is not produced by the action of dil. HNO_3 on (V), which gives solely (VI) and (VII). 2-Iodocyclopentanol, from HOI and cyclopentene, is almost exclusively transformed by AgNO_3 into the corresponding epoxide, which is hydrated by HNO_3 produced simultaneously to the glycol without isomerisation into cyclopentanone or cyclobutylformaldehyde. 2-Iodocyclohexanol and 2-iodo-4-methylcyclohexanol are transformed in 30% yield into cyclopentylformaldehyde and 3-methylcyclopentylformaldehyde, respectively; the corresponding glycol (VIII) (20—40%) and its nitrate also result. (VIII) is formed by hydration by dil. HNO_3 of the initial epoxide, which is almost the sole product from the iodohydrin and Ag_2O . H. W.

Structure of β -sitosterol and its preparation from stigmasterol. S. BERNSTEIN and E. S. WALLIS (J. Org. Chem., 1937, 2, 341—345).—Bengtsson's results (A., 1936, 69) indicate that β -sitosterol (I) should be identical with 22-dihydrostigmasterol (II). This is confirmed by prep. of (II) by side-chain hydrogenation (H_2 -Pd) of stigmasteryl acetate, hydrolysis, and removal of small amounts of sterols hydrogenated in the 5:6 position by conversion of the product into the *p*-toluenesulphonates and hydrolysis (aq. COMe_2), when (II) alone is regenerated. Physical data for (II) and its derivatives approximate closely to those for (I) from cottonseed oil and its corresponding derivatives. Hydrogenation (H_2 -PtO₂) of (I) gives stigmastanol. E. G. B.

Δ^4 -Androstene-3:17-diol. A. BUTENANDT and A. HEUSNER [with, in part, D. VON DRESLER and U. MEINERTS] (Ber., 1938, 71, [B], 198—204).—Testosterone behaves like cholesterol (I) towards $\text{Al}(\text{OPr}^i)_3$ in boiling Pr^iOH since it is reduced to a mixture of *n*- (II), m.p. 153—154°, $[\alpha]_D^{25} +48.52^\circ$ in EtOH, and *epi*- (III), m.p. 202—206°, $[\alpha]_D^{25} +187.5^\circ$ in $\text{C}_5\text{H}_5\text{N}$, Δ^4 -androstenediol (cf. A), separable by pptn.



of (II) by digitonin from EtOH. The diacetates of (II) and (III) have m.p. 101—102° and 121°, respectively. (II) and (III) give a marked red colour with $\text{CCl}_3\text{-CO}_2\text{H}$ and their physical properties in comparison with the Δ^4 -unsaturated reduction products of (I) and the corresponding steroids show that displacement of the double linking from Δ^5 towards Δ^4 is accompanied by inversion of sign of optical rotation. Treatment of (II) with boiling 95% EtOH containing a little conc. HCl gives $\Delta^{3:5}$ -androstadien-17-ol (+0.5 H_2O) (IV), m.p. 146°, the acetate, m.p. 122—123°, $[\alpha]_D^{25} -147.4^\circ$ in EtOH, of which is also obtained from (III) and Ac_2O at 100°. The physiological action of (II) and (III) is described. Dehydration of Δ^5 -androstenediol by anhyd. CuSO_4 gives (IV), which is also obtained by reduction $[\text{Al}(\text{OPr}^i)_3]$ of $\Delta^{3:5}$ -androstadienone. H. W.

Sterols. XXVIII. Pregnanetriols from pregnancy urine. R. E. MARKER, O. KAMM, H. M. CROOKS, T. S. OAKWOOD, E. L. WITTLE, and E. J. LAWSON (J. Amer. Chem. Soc., 1938, 60, 210—211; cf. A., 1938, II, 58).—Mares' pregnancy urine affords pregnanetriol-A (10 mg. per gallon), $\text{C}_{27}\text{H}_{46}\text{O}_3$, m.p. 295—300° (triacetate, m.p. 136°), and -B (6 mg. per gallon), m.p. 300—302°, $[\alpha]_D^{25} -41^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (triacetate, m.p. 168°), best purified by way of the acetates: -A and -B may be related as are pregnanediol and allopregnanediol. -B may be identical with the compound of Haslewood *et al.* (A., 1934, 1126). -A and -B give no ppt. with digitonin and contain an angular Me since they give no C_{10}H_8 derivative with Pt-black at 300°. One OH in -A is at C_{20} , probably as $\text{CHMe}\cdot\text{OH}$, since the CHI_3 reaction is positive; a second OH is probably at C_{3} ; the third, probably not *tert.* as it can be acetylated, is probably in the same position as the unreactive nuclear OH of the cortical hormone derivative of Reichstein (A., 1936, 1383). R. S. C.

Normal long-chain acids terminating in cyclohexyl or cyclopentyl. II. cyclopentylvaleric acid and its derivatives. M. M. KATZNELSON and M. S. KONDAKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1937, 17, 367—370).—Mg cyclopentyl bromide and furfuraldehyde yield cyclopentylfurfurylcarbinol, b.p. 114—116°/8 mm., converted by EtOH-HCl into the Et ester, b.p. 140—147°/9 mm., of δ -cyclopentyl-lævulic acid, m.p. 65°. Reduction (Clemmensen) of this ester gives the -valeric acid, m.p. 11°, b.p. 150—153°/9 mm. (Me ester, b.p. 118—119°/12 mm.; chloride, b.p. 124°/12 mm.; amide, m.p. 138°; anilide, m.p. 81—81.5°; Cd salt). A. Li.

cyclopentyl- and cyclohexyl-succinic acids and resolution of cyclopentylsuccinic acid. S. K. RANGANATHAN (Current Sci., 1937, 6, 277—278).—Et sodio- α -carbethoxysuccinate condenses with cyclopentyl and cyclohexyl bromides to give respectively Et α -carbethoxy- α -cyclopentyl-, b.p. 166°/45 mm., and - α -cyclohexyl-succinate, b.p. 168°/45 mm. Hydrolysis and decarboxylation yields cyclopentyl- (I), m.p. 117° (anhydride, b.p. 176°/30 mm.; Et ester, b.p. 142°/6 mm.), and cyclohexyl-succinic acid, m.p. 143°. (I) has been resolved through the brucine salt into the *d*-, m.p. 135°, $[\alpha]_D^{25} +17.81^\circ$, and *l*-acids, m.p. 135°, $[\alpha]_D^{25} -16.94^\circ$ (in COMe_2). F. R. S.

Alkoxyalkyl esters of alicyclic carboxylic acids.—See B., 1938, 140.

m-Xylylacetic acid and its derivatives. J. V. HARISPE (Bull. Inst. Pin, 1937, 155—173, 195—216).—An account of work reviewed previously (A., 1936, 992, 1506). H. W.

Rôle of the acetyl derivative as an intermediary stage in the biological synthesis of amino- from keto-acids. V. DU VIGNEAUD and O. J. IRISH (J. Biol. Chem., 1938, 122, 349—370).—Biological conversion of (–) into (+)- α -amino- γ -phenylbutyric acid in the dog is demonstrated, and the hypothesis of Knoop (A., 1911, ii, 514) of oxidation via the Ac derivative to the CO-acid and subsequent asymmetric synthesis of the NHAc-acid (by reaction with AcCO_2H and NH_3) is confirmed. The results with the *dl*-acid are confirmed. When the (–) or (+)-acid is fed to dogs, (+)- α -acetamido- γ -phenylbutyric acid (with some hydroxy-acid and hippuric acid), which corresponds with the (+)- NH_2 -acid (I), is excreted. Feeding of *dl*- α -acetamido- γ -phenylbutyric acid leads to excretion of excess of the (–)-form, showing biological hydrolysis of the (+)-isomeride. (I) is shown to correspond with the naturally occurring NH_2 -acids by Lutz and Jirgensons' method (A., 1930, 460), and should therefore be renamed 1-(+)- α -amino- γ -phenylbutyric acid. Preliminary metabolic experiments with *dl*-acetylphenylalanine showed that a larger amount of the (–)-Ac derivative is excreted, confirming the results of Knoop and Blanco (A., 1925, i, 1208), but not their conclusion that the original hypothesis (above) should be abandoned, since the (–)-Ac derivative corresponds with (+), not (–)-phenylalanine. The above results reinstate the AcCO_2H -acetylation theory for the synthesis *in vivo* of NH_2 -acids, which is discussed.

$\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$ is brominated and converted by NH_3 into *dl*- α -amino- γ -phenylbutyric acid, m.p. 305—306°, of which the formyl derivative, m.p. 130—131° [*brucine* salt, m.p. 160—162°, $[\alpha]_D^{20} = -23.2^\circ$ in MeOH, of the (–)-form], is resolved and hydrolysed to (–), m.p. 323—325°, $[\alpha]_D^{20} = -47.0^\circ$ in *N*-HCl, and (+)- α -amino- γ -phenylbutyric acid, m.p. 326—328°, $[\alpha]_D^{20} = +48.8^\circ$ in *N*-HCl [Ac derivative, m.p. 179—180°, $[\alpha]_D^{20} = +26.7^\circ$ in EtOH, also obtained biologically (see above)]. M.p. are corr. E. W. W.

Hexadeuterobenzene as solvent for optically active substances. H. ERLÉNMEYER and H. SCHENKEL (Helv. Chim. Acta, 1938, 21, 114).—Me (+)-mandelate has $[\alpha]_D^{20} = +174.78 \pm 0.13^\circ$ $[\alpha]_{D_{105.6}}^{20} = +252.88 \pm 0.13^\circ$ in C_6H_6 and $[\alpha]_D^{20} = +173.44 \pm 0.26^\circ$ and $[\alpha]_{D_{105.6}}^{20} = +251.32 \pm 0.26^\circ$ in C_6D_6 . H. W.

2-Chloro-4 : 5- and -5 : 6-diaminobenzoic acid. H. GOLDSTEIN and A. STUDER (Helv. Chim. Acta, 1938, 21, 51—56).—Reduction of 4 : 5 : 2-(NO_2) $_2\text{C}_6\text{H}_2\text{Cl}\cdot\text{CO}_2\text{H}$ with SnCl_2 and conc. HCl gives 2-chloro-4 : 5-diaminobenzoic acid, m.p. 219° [dihydrochloride (I); Ac_2 derivative, m.p. about 242° (decomp.)], slowly converted by boiling glacial AcOH into 6-chloro-2-methylbenzimidazole-5-carboxylic acid, m.p. about 324° (decomp.). Treatment of (I) with HNO_2 leads to 6-chlorobenzotriazole-5-carboxylic acid, m.p. about 320° (decomp.). With Ac_2 and

benzil, (I) gives 7-chloro-2 : 3-dimethyl-, m.p. 260°, and 7-chloro-2 : 3-diphenyl-quinoxaline-6-carboxylic acid, m.p. 247° (decomp.), respectively. 5 : 2- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{H}$ is reduced by SnCl_2 and conc. HCl to 5 : 2- $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{H}$, the Ac derivative, m.p. 216.5°, of which is converted by HNO_3 (*d* 1.52) at 50—60° into 2-chloro-6-nitro-5-acetamidobenzoic acid, m.p. 236° (decomp.). This is hydrolysed by 10% KOH to 2-chloro-6-nitro-5-aminobenzoic acid, m.p. 202°, reduced (SnCl_2 and conc. HCl) to 2-chloro-5 : 6-diaminobenzoic acid (II) [dihydrochloride; Ac_2 derivative, m.p. about 242° (decomp.)]. The constitution of (II) rests on the established presence of 2 NH_2 in the *ortho*-position to one another and on its difference from the known 2-chloro-4 : 5- or -3 : 5-diamino-acids. (II) is condensed with Ac_2 and benzil to 6-chloro-2 : 3-dimethyl-, m.p. 278° (decomp.), and with benzil to 6-chloro-2 : 3-diphenyl-quinoxaline-5-carboxylic acid, m.p. 248°, respectively. M.p. are corr. H. W.

Synthesis of sympathomimetically active local anaesthetics. K. H. SLOTTA and R. KETHUR (Ber., 1938, 71, [B], 59—63).— $m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ is transformed (diazo-method) into $m\text{-CN}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, which with MeNO_2 in presence of KOH gives ω -nitro-*m*-cyanostyrene in 42.5% yield. This is converted by HCl in MeOH-Et₂O into the hydrochloride, m.p. 151°, of the methyliminoether of ω -nitrostyrene-*m*-carboxylic acid from which little (I) (below) could be obtained. $p\text{-CHO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ condenses with MeNO_2 in presence of KOH to *Me p*- ω -nitrovinylbenzoate, m.p. 178°, obtained in smaller yield by use of NH_3MgCl as condensing agent. It is reduced electrolytically at a Pb electrode to *Me p*- β -aminoethylbenzoate hydrochloride, m.p. 208—211°. Similarly $p\text{-CHO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ affords successively *Et p*- ω -nitrovinylbenzoate, m.p. 112°, and *Et p*- β -aminoethylbenzoate hydrochloride, m.p. 178°, which, like the Me ester, is a powerful anaesthetic. $m\text{-CHO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ similarly gives *Me m*- ω -nitrovinylbenzoate (I), m.p. 119°, in 69.7% yield, electrolytically reduced to *Me m*- β -aminoethylbenzoate hydrochloride, m.p. 142°; the corresponding *Et* esters have m.p. 109° and 114°, respectively. The *m*-derivatives are not anaesthetics. H. W.

Action of mixed organo-magnesium compounds on hydroxy- or alkoxy-aromatic amides. P. COUTURIER (Compt. rend., 1937, 205, 800—802; cf. A., 1927, 875).—2 : 4-(OAc) $_2\text{C}_6\text{H}_3\cdot\text{COCl}$ with NHEt_2 affords 2 : 4-diacetoxybenzdiethylamide, m.p. 79°, hydrolysed (dil. NaOH) to β -resorcyldiethylamide (I), m.p. 142°, which with MgEtBr (5 mols.) in boiling C_6H_6 gives a 10% yield of 2 : 4-(OH) $_2\text{C}_6\text{H}_3\cdot\text{COEt}$; (I) is intermediate in reactivity between an *o*- and *p*-OH-compound. Similarly *o*- (II), b.p. 170°/17 mm., and *p*-methoxy- (III), 3 : 4-dimethoxy-, and 3 : 4 : 5-trimethoxy-benzdiethylamide with MgEtBr afford the corresponding propiophenones in 60—80% yield. In addition (II) and (III) (cf. A., 1936, 1107) afford basic products [*picrate* of that from (III) has m.p. 115° (decomp.)]. (III) with MgPhBr in boiling C_6H_6 affords no ketone but (diphenyl-*p*-anisylmethyl)diethylamine, b.p. 117°/3 mm. converted by dil. acid into diphenyl-*p*-anisylcarbinol and NHEt_2 . *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$ and 3 : 4 : 5-(OMe) $_3\text{C}_6\text{H}_2\cdot\text{CO}\cdot\text{NH}_2$

react similarly with MgEtBr to give propiophenones (70%) together with *p*-methoxy-, m.p. 45° and 3 : 4 : 5-trimethoxy-propiophenoneimine, m.p. 48°, which are easily hydrolysed (HCl) and when heated under pressure give NH_3 .

J. L. D.

γ -Chloropropyl imidobenzoate [α -iminobenzyl γ -chloropropyl ether] hydrochloride. J. B. CLOKE and F. A. KENISTON (J. Amer. Chem. Soc., 1938, 60, 129—131).— PhCN , $\text{Cl} \cdot [\text{CH}_2]_3 \cdot \text{OH}$, and HCl in Et_2O at 0° give α -iminobenzyl γ -chloropropyl ether hydrochloride (I), m.p. 116·2°; some dihydrochloride [converted when kept over soda-lime and CaO in a vac. into (I)] is also formed. With H_2O (I) gives only $\text{Cl} \cdot [\text{CH}_2]_3 \cdot \text{OBz}$, b.p. 154—156°/22 mm., the hydrolysis being unimol., $k = 0.00784$ at 28°; the γ -Cl accelerates the reaction as compared with that of $\text{OPr}^n \cdot \text{CPh} \cdot \text{NH}_2 \cdot \text{Cl}$. When heated, (I) gives NH_2Bz and $[\text{CH}_2]_3\text{Cl}_2$. The free imine rearranges to $\text{Cl} \cdot [\text{CH}_2]_3 \cdot \text{NHBz}$ and μ -phenylpentoxazoline hydrochloride.

R. S. C.

Electrosynthesis of methyl dicyclohexyl-4 : 4'-dicarboxylate from methyl hydrogen *trans*-hexahydroterephthalate. F. FICHTER and T. HOLBRO (Helv. Chim. Acta, 1938, 21, 141—151).—The inability of $\text{Me H trans-hexahydroterephthalate}$ to undergo Kolbe's electrosynthesis is attributed to hindrance due to the proximity of the CO_2H groups since similar difficulties are not encountered with the corresponding terephthalate. $p\text{-C}_6\text{H}_4(\text{CO}_2\text{Me})_2$ is hydrogenated (Pt-black in AcOH) to a mixture from which $\text{Me}_2 \text{ trans-hexahydroterephthalate}$, m.p. 71°, separates. Hydrolysis of the residual ester mixture and treatment of the acids with conc. HCl at 120° gives the pure *trans*-acid, smoothly esterified by $\text{MeOH-H}_2\text{SO}_4$ and then partly hydrolysed to $\text{Me H trans-hexahydroterephthalate}$, m.p. 126°. Electrolysis of $K \text{ Me trans-hexahydroterephthalate}$ in MeOH with Pt anode and Cu cathode gives $\text{Me}_2 \text{ dodecahydrodiphenyl-4 : 4'-dicarboxylate}$ (I), m.p. 100—101°, accompanied by $\text{Me } \Delta^3\text{-cyclohexenecarboxylate}$ containing a small proportion of $\text{Me hexahydrobenzoate}$. (I) is hydrolysed by $\text{KOH-MeOH-H}_2\text{O}$ to a mixture (II) of acids, $\text{C}_{14}\text{H}_{22}\text{O}_4$, m.p. 245—250° after gradual darkening above 200° (corresponding *Ba* salt). Treatment of (II) with conc. HCl at 180° leads to *trans-trans-dodecahydrodiphenyl-4 : 4'-dicarboxylic acid*, m.p. about 345° (Me_2 ester, m.p. 117°).

H. W.

Action of organomagnesium compounds on *o*-NN-diethylphthalamic acid. N. MAXIM and (MLLE.) A. ANDREESCU (Bull. Soc. chim., 1938, [v], 5, 54—57; cf. A., 1928, 519).—Interaction of $\text{o-NEt}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ (I) with Mg alkyl or aryl halides provides a general method of prep. of phthalides in good yield; $\text{o-XMg} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CR}_2 \cdot \text{O} \cdot \text{MgX}$ and NHEt_2 are first formed, the former being hydrolysed to $\text{o-CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CR}_2 \cdot \text{OH}$, which then loses H_2O yielding phthalides. Thus are prepared di-*n*-propyl-, diisobutyl-, diisomyl-, b.p. 196°/12 mm., dibenzyl-, and diphenyl-phthalides.

E. G. B.

5-Bromo- and 5-chloro-2-naphthoic acid. H. GOLDSTEIN and R. MATTHEY (Helv. Chim. Acta, 1938, 21, 62—66).—5 : 2- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{CN}$ (I) is transformed by Sandmeyer's reaction into 5 : 2- $\text{C}_{10}\text{H}_6 \cdot \text{Br} \cdot \text{CN}$,

m.p. 154°, identical with the compound obtained by bromination of 2- $\text{C}_{10}\text{H}_7 \cdot \text{CN}$, and hydrolysed by boiling $\text{H}_2\text{SO}_4\text{-AcOH-H}_2\text{O}$ to 5-bromo-2-naphthoic acid (II), m.p. 270°, identical with the product of the direct bromination of 2- $\text{C}_{10}\text{H}_7 \cdot \text{CO}_2\text{H}$. (II) gives a *Me* ester, m.p. 73°, a *chloride*, m.p. 83°, *amide*, m.p. 195°, and *anilide*, m.p. 202·5°. Similarly (I) is transformed into 5 : 2- $\text{C}_{10}\text{H}_6 \cdot \text{Cl} \cdot \text{CN}$, identical with that obtained by the chlorination of 2- $\text{C}_{10}\text{H}_7 \cdot \text{CN}$ and hydrolysed to 5-chloro-2-naphthoic acid (III), m.p. 270° (*Me* ester, m.p. 81°; *chloride*, m.p. 89°; *amide*, m.p. 190·5°; *anilide*, m.p. 202·5°). The m.p. of (II) and (III) are identical and nearly the same as that of their mixtures. The graph showing the relationship between m.p. and composition of mixtures of (II) and (III) is nearly a horizontal straight line. M.p. are corr.

H. W.

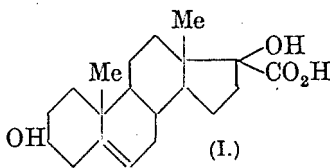
Synthesis of 1-hydroxy-2-naphthonitrile. J. A. MCRAE and L. MARION (Canad. J. Res., 1937, 15, B, 480—485).— $\text{CH}_2\text{Ph} \cdot \text{CHO}$ (I) and $\text{CN} \cdot \text{CHNa} \cdot \text{CO}_2\text{Et}$ in EtOH give $\alpha\alpha'$ -dicyano- β -benzylglutaric acid, m.p. 168° (lit. 173°) [also formed from (I) and aq. $\text{CN} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Na}$], and (probably) $\text{Et } \alpha$ -cyano- β -benzylacrylate, b.p. 182°/15 mm. The latter when distilled at 2—4 mm. loses EtOH and forms 1-hydroxy-2-naphthonitrile (II), m.p. 179° (*Me ether*, m.p. 50—51°; 4-*p*-nitrobenzeneazoderivative, m.p. 275°), also obtained from 1 : 2- $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CH} \cdot \text{N} \cdot \text{OH}$ and aq. EtOH-KCN . (II) and BzCl in $\text{C}_6\text{H}_5\text{N}$ give a compound, m.p. 159—160°. Contrary to Linstead and Williams (A., 1926, 1245), (I) is oxidised by AcOH-CrO_3 to BzOH . M.p. are corr.

D. E. W.

Sex hormones. XXVIII. Preparation of Δ^5 -3-*trans*-17-dihydroxy Δ^5 tiocolenic acid from Δ^5 -*trans*dehydroandrosterone. L. RUZICKA and K. HOFMANN (Helv. Chim. Acta, 1938, 21, 88—93).—Treatment of Δ^5 -17-hydroxy-3-*trans*acetoxy-17-ethinylandrostene with Br in CCl_4 followed by ozonisation and treatment of the product with H_2O affords, after esterification, *Me* Δ^5 -17-hydroxy-3-*trans*acetoxy Δ^5 tiocolenate, m.p. 163—164°, hydrolysed to Δ^5 -3-*trans*-17-dihydroxy Δ^5 tiocolenic acid (I), m.p. 260—261° (decomp.) [*Me* ester (II), m.p. 190—191°], and *trans*-dehydroandrosterone acetate, m.p. 171—172° [*semicarbazone*, m.p. about 270° (decomp.)]. (I) is treated successively with Br and CrO_3 in AcOH at room temp. and then debrominated by Zn dust to Δ^4 -androstene-3 : 17-dione, m.p. 172—173°. (II) is transformed by cold $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$ into its acetate, m.p. 201—202°. Δ^5 -3-*trans*-17-Diacetoxy Δ^5 tiocolenic acid, m.p. 220—220·5°, and its *Me* ester, m.p. 145—145·5°, are described. M.p. are corr.

H. W.

Bile acids. LIII. M. SCHENCK (Z. physiol. Chem., 1938, 251, 32—40; cf. A., 1937, II, 420).—The isonitroketo-acid, $\text{C}_{24}\text{H}_{33}\text{O}_{10}\text{N}$, yields a *dioxime*, whilst the α -acid, $\text{C}_{24}\text{H}_{34}\text{O}_{10}\text{N}_2$, and the ketolactam-tricarboxylic acid, $\text{C}_{24}\text{H}_{35}\text{O}_{10}\text{N}$, yield *monoximes* with NH_2OH . Bilisoidanic acid appears to yield a *trioxime* and hence is probably a triketotricarboxylic



acid; oximation in alkaline solution gives the monoxime of the "benzilic acid rearrangement" product (cf. A., 1927, 1080). The β -acid, $C_{21}H_{34}O_{10}N_2$, yields no oxime with NH_2OH . The possible structures of the acids are discussed in the light of these results.

W. McC.

Catalytic hydrogenation of cinnamaldehyde and of citronellal. [Nickel as catalyst of the Cannizzaro reaction.] M. DELÉPINE and C. HANE-GRAFF (Bull. Soc. chim., 1937, [v], 4, 2087—2093).—In addition to results previously recorded (A., 1937, II, 421), $CH_2Ph \cdot CH_2 \cdot CHO$ gives, on keeping, a trimeride, m.p. 64° . Discrepancies between unsaturation of citronellal (I) and H_2 absorbed when Ni is used are due to a Cannizzaro reaction. With Ni in $EtOH$ or Et_2O , (I) yields citronellol and Ni citronellate. Similarly Pr^iCHO and Ni in H_2O yield Bu^iOH and $(Pr^iCO_2)_2Ni$. The reaction can be represented: $5RCHO + Ni + 2H_2O \rightarrow (RCO_2)_2Ni + 3CH_2R \cdot OH$, the Cannizzaro reaction being accompanied by reduction by Ni.

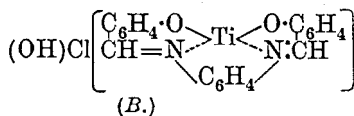
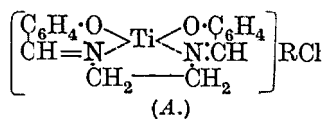
E. W. W.

Reducing action of alkali benzyloxides on hydratropaldehyde and α -alkylcinnamaldehydes. P. MASTAGLI (Compt. rend., 1937, 205, 802—805; cf. A., 1937, II, 102).—Hydratropaldehyde or its *p*-Me derivative, in boiling $2N \cdot CH_2Ph \cdot OH \cdot KOH$ (I) or $-NaOH$ (II), affords the corresponding alcohol, H_2 , and $BzOH$. β -Phenyl-, b.p. $116^\circ/18$ mm. (*allophanate*, m.p. 175°), and β -*p*-tolyl-propyl alcohol, b.p. $124^\circ/17$ mm. (*allophanate*, m.p. 157°), are described. $\alpha\beta$ -Unsaturated aldehydes are converted into saturated alcohols by (I) but not by (II) at 100° . α -Ethylcinnamaldehyde with (II) at 100° gives β -ethylcinnamyl alcohol (*allophanate*, m.p. 147°) and $NaOBz$; at 200° the saturated alcohol is formed. The following are prepared similarly (m.p. of *allophanates* in parentheses): β -*n*-butyl-, b.p. $155^\circ/15$ mm. (155°); α -methyl-, b.p. 160° ; α -hexyl-, b.p. $176^\circ/15$ mm. (142°); α -octyl-, b.p. $198^\circ/15$ mm. (138°); α -nonyl-, b.p. $212^\circ/17$ mm. (132°); α -nonenyl-, b.p. $212^\circ/17$ mm. (127°); and α -decyl-cinnamyl alcohol, b.p. $221^\circ/15$ mm., m.p. 42° (137°).

J. L. D.

Reaction of vanillin and salicylaldehyde with acetone.—See A., I, 147.

Internally complex titanium salts. P. PFEIFFER and H. THIELERT (Ber., 1938, 71, [B], 119—123).—Cautious addition of salicylaldehyde-ethylene-



di-imine in C_5H_5N to $TiCl_4$ in C_5H_5N gives basic *Ti* salicylaldehyde-ethylenedi-imine chloride (I) (A; R = OH), which dissolves without decomp. in H_2O giving a solution in which Cl can be quantitatively pptd. by $AgNO_3$. The corresponding nitrate, decomp. 245° , and perchlorate result on addition of the requisite acid. With conc. H_2SO_4 (I) evolves HCl copiously, thus confirming the ionoid nature of Cl. The position of OH is uncertain and it is placed outside the complex radical for convenience. The production of an acetate (A; R = OAc) from (I) and Ac_2O throws no light on

the problem. Similarly salicylaldehyde-*o*-phenylene-di-imine gives the substance B, whence the corresponding perchlorate.

H. W.

Synthesis of *p*-cyclohexylbenzaldehyde and *p*-cyclohexylbenzoic acid. D. BODROUX and R. THOMASSIN (Compt. rend., 1937, 205, 991—993).—*p*-cyclohexylbromobenzene (improved prep.) and Mg in Et_2O yield Mg *p*-cyclohexylphenyl bromide (I), and a little 4:4'-dicyclohexyldiphenyl, m.p. 202 — 203° . Interaction of (I) and $CH(OEt)_3$ followed by hydrolysis (dil. HCl) yields *p*-cyclohexylbenzaldehyde, whilst (I) with solid CO_2 in Et_2O gives *p*-cyclohexylbenzoic acid (61% yield; with gaseous CO_2 the yield is very poor), oxidised ($KMnO_4$) to p - $C_6H_4(CO_2H)_2$.

J. D. R.

Two stereoisomeric *dl*-dihydrocamphorones. R. CALAS (Compt. rend., 1938, 206, 59—61).—2-Methyl-5-isopropyl- Δ^4 -cyclopentenone (I) with H_2 -Raney Ni in neutral or alkaline solution gives trans- (II), b.p. $179.8^\circ/766$ mm. [*semicarbazone*, m.p. 209° ; *oxime*, b.p. $117^\circ/16$ mm.; *carbanilidoxime*, a liquid and m.p. 139° (two forms)], and cis-2-methyl-5-isopropylcyclopentanone (III), b.p. $179.7^\circ/766$ mm. [*semicarbazone*, m.p. 198° ; *oxime*, b.p. 118 — $119^\circ/15$ mm.; *carbanilidoxime*, m.p. 78° and 142° (two forms)]; the configurations are deduced from the fact that (II) reacts with NH_2OH and is reduced (Na in Et_2O - H_2O) more readily than (III). (I) with H_2 -Pt-black in neutral solution affords (II), whereas in $AcOH$, (III) is formed. The Raman spectra of (II) and (III) are identical.

J. L. D.

Syntheses with β -chloroethyl and β -vinyl ketones. Preparation of Δ^2 -cyclohexenones. J. DÉCOMBE (Compt. rend., 1937, 205, 680—682; cf. A., 1936, 1094, 1490).— α -Substituted derivatives (I) of β -chloroethyl and β -vinyl ketones differ from the parent ketones in reduced mobility of halogen atom and in mol. refraction. Blaise-Maire condensation of $COEt \cdot CH_2 \cdot CH_2Cl$ with $CH_3Ac \cdot CO_2Et$ to give 3-methyl- Δ^2 -cyclohexenone (A., 1908, i, 390) can be generalised for (I). Thus (I) with β -ketoic esters yield diketo-esters (II), which on hydrolysis [$Ba(OH)_2$] give Δ^2 -cyclohexenones (yield from β -ketoic esters, 35—55%) by way of the 6- CO_2Et derivatives. (II) could not be isolated pure since on distillation they partly cyclise to decarboxylated products. The following are described. 3:4-Dimethyl-, b.p. 92 — $95^\circ/15$ mm. [*oxime*, b.p. 132 — $135^\circ/15$ mm. (lit. m.p. 105 — 109°) (benzoate, m.p. 112 — 113°)], 3-methyl-6-ethyl-, b.p. 95 — $98^\circ/12$ mm. [*oxime*, b.p. 135 — $140^\circ/15$ mm. (*p*-nitrobenzoate, m.p. 193°)], 4-methyl-3-ethyl-, b.p. 99 — $104^\circ/15$ mm. [*oxime*, b.p. 143 — $148^\circ/16$ mm. (benzoate, m.p. 76°)], 2:4-dimethyl-3-ethyl-, b.p. 105 — $106^\circ/15$ mm. (*oxime*, m.p. 68°), 4-methyl-3:6-diethyl-, b.p. 122 — $127^\circ/15$ mm. (*oxime*, b.p. 152 — $154^\circ/15$ mm.), and 2:4:6-trimethyl-3-ethyl-, b.p. 118 — $121^\circ/15$ mm. [*oxime*, b.p. 150 — $152^\circ/15$ mm. (*p*-nitrobenzoate, m.p. 106°)], Δ^2 -cyclohexenones.

E. G. B.

Mechanism of ketolisation by mixed amino-magnesium compounds. J. COLONGE (Bull. Soc. chim., 1938, [v], 5, 98—102; cf. A., 1934, 1359).—2:2:6:6-Tetramethylcyclohexanone (I) [prepared by successive methylation ($NaNH_2$ -MeI or Me_2SO_4)

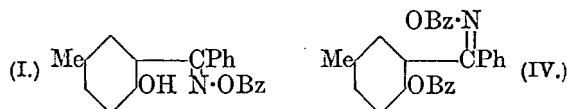
of 2-methylcyclohexanone], which cannot enolise, does not react with $\text{NPhMe}\cdot\text{MgBr}$, and when COMeBu^* is added to the mixture, only $\text{COBu}^*\cdot\text{CH}_2\cdot\text{CMeBu}^*\cdot\text{OH}$ is formed; (I) is recovered unchanged. The non-condensation of (I) to a OH-ketone is due to steric hindrance; previous results (A., 1933, 698) can be similarly explained without postulating enolisation of the ketone by the Mg derivative. E. G. B.

Prototropy in relation to the exchange of hydrogen isotopes. III. Comparison of the rates of racemisation and of hydrogen exchange in a ψ -acidic ketone. S. K. HSÜ, C. K. INGOLD, and C. L. WILSON (J.C.S., 1938, 78—81).—According to the ionisation theory of prototropy, the rate of isomerisation of ψ -acids is equal to the rate of ionisation, since equilibrium between a ψ -acid and its ions is established slowly relatively to that between the ions and the true acid. Since H exchange depends on H ionisation, comparison of rates of H exchange and of isomerisation provides a test for the above theory. The rate of isomerisation, *i.e.*, of enolisation, of a ψ -acidic ketone is measured by bromination or by racemisation, and the rate of H exchange by D uptake, all measurements being made in the same protium-free D solvent. $l\text{-COPh}\cdot\text{CHMeEt}$, b.p. $64^\circ/0.02\text{ mm.}$, with NaOD in 2 : 1 dioxan- D_2O at 35° shows equal rates of racemisation and of H exchange. From this and previous results it is concluded that bromination, racemisation, and H exchange of an enolisable ketone are all controlled by its ionisation. E. G. B.

Oximation of aldehydes and ketones. G. VAVON and P. ANZIANI [in part with P. AUBERTEIN] (Bull. Soc. chim., 1937, [v], 4, 2026—2037).—Velocity (v) of oxime formation is a min. with equimol. amounts of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and NaOH, except with phenolic aldehydes, which require excess of NaOH. Ratios of max. to min. v may be very great (600 for vanillin). Steric hindrance reduces v , *e.g.*, in substituted acetophenones. A mixture of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and NH_2OH is a stable and effective reagent, permitting the prep. of dimethylallyl-, m.p. 126° , methylethylallyl-, m.p. 92° ($98^\circ?$), ethylallyl-, m.p. 138° , and diethylallyl-acetophenoneoxime, m.p. 130° . Aldehydes with *o*-OH have much greater v than those with *m*- or *p*-OH; chelation is supposed. Oxime formation with terpene ketones is studied, and an improved prep. of fenchoneoxime, m.p. $164\text{—}165^\circ$, is described. E. W. W.

Chemical effects accompanying hydrogen bonding. I. Acyl derivatives of the 2-hydroxy-5-methylbenzophenoneoximes [phenyl 4-hydroxy-*m*-tolyl ketoximes]. A. H. BLATT (J. Amer. Chem. Soc., 1938, 60, 205—210).—Differences in behaviour of *syn*- and *anti*-*o*-hydroxybenzophenoneoximes are ascribed to the presence or absence of OH·N linkings, because such differences are destroyed by acylation of the phenolic OH or by salt formation. In general H-linkings have less effect on chemical properties than have other linkings since the energy needed to break them is less. *syn*-Ph 4-hydroxy-*m*-tolyl ketoxime benzoate (I), m.p. $148\text{—}149^\circ$, is hydrolysed to the parent oxime by NaOH, rearranged to 1-phenyl-4-methylbenzoxazole (II) by Na_2CO_3 , and converted by pyrolysis into 2-phenyl-4-methyliso-

benzoxazole. The corresponding *anti*-oxime benzoate (III), m.p. $174\text{—}175^\circ$, is hydrolysed to the *anti*-oxime by NaOH or Na_2CO_3 , and pyrolysis gives (II) in very poor yield. These reactions resemble those of the acetates (A., 1936, 1511), except that the



anti-oxime acetate gives a mixture of oxazole and isoxazole when pyrolysed; the latter product is considered to result from a change of configuration prior to pyrolysis. The dibenzoate, m.p. $147\text{—}148^\circ$, of the *syn*-oxime resembles the *anti*-monobenzoate in being hydrolysed without rearrangement by NaOH or Na_2CO_3 ; under mild conditions *syn*-Ph 4-benzoyloxy-*m*-tolyl ketoxime (A), m.p. $162\text{—}163^\circ$, is obtained. The dibenzoate, m.p. $132\text{—}133^\circ$, of the *anti*-oxime is unaffected by Na_2CO_3 , but is hydrolysed by NaOH either to the oxime or to (III); formation of (III) proves the configuration (IV), since in the alternative (V) the $\text{BzO}\cdot\text{N}$ would be sterically protected from attack. Absence of H-bonding in (A) is shown by its giving 4 : 1 : 3-OBz· $\text{C}_6\text{H}_3\text{Me}\cdot\text{NHBz}$ and not the benzoxazole on Beckmann rearrangement.

With AcCl at room temp. the *syn*-oxime gives (II); at the b.p. it gives the *syn*-acetate (free phenolic OH) or very slowly by rearrangement the *anti*-diacetate, m.p. 100° , which is obtained very readily (hot or cold) from the *anti*-oxime or its monoacetate, and is hydrolysed to the *anti*-oxime by acids or alkali. The oximes or their acetates all give 4 : 1 : 3- $\text{OAc}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NHBz}$ when treated with $\text{Ac}_2\text{O}\text{—}\text{H}_2\text{SO}_4$. With PhSO_2Cl in $\text{C}_5\text{H}_5\text{N}$ or 20% aq. KOH the *anti*-oxime gives 4 : 1 : 3- $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{NHPH}$, but the *syn*-oxime affords (II) in $\text{C}_5\text{H}_5\text{N}$ and the isobenzoxazole in 20% KOH, which shows the destruction of the H-linking by salt-formation. *syn*-Ph 4-hydroxy-*m*-tolyl ketoxime 2 : 4 : 6-trimethylbenzoate [structure as (I)], m.p. $108\text{—}109^\circ$ or $149\text{—}150^\circ$, gives (II) with Na_2CO_3 or NaOH and the isobenzoxazole when pyrolysed. The anti-2 : 4 : 6-trimethylbenzoate, m.p. $176\text{—}177^\circ$, decomposes when pyrolysed, resists ordinary treatment with alkali, but furnishes (II) by long treatment with NaOH. Thus formation of (II) and hydrolysis occur by different mechanisms; the former is favoured by H-linkings and may be brought into prominence by preventing sterically the addition necessary for hydrolysis. R. S. C.

Substituted benzophenoneimines.—See B., 1938, 140.

Tautomerisation of an optically active azomethine. G. T. BORCHERT and H. ADKINS (J. Amer. Chem. Soc., 1938, 60, 3—6).—The rate of isomerisation of *l*- $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CPh}\cdot\text{N}\cdot\text{CHPhMe}$ (I), $[\alpha]_{\text{D}}^{25} -19.5^\circ$, $[\alpha]_{\text{D}}^{25} -26.3^\circ$ in EtOH, is determined (a) by decrease in α and (b) by hydrolysis of the mixture formed and determination of the resultant mixed ketones by the polarograph. The methods give identical results, $k_1 = 0.00635\text{ hr.}^{-1}$, showing that the isomeric azomethines are in dynamic equilibrium

with each other. $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{COPh}$, m.p. 75.5–76°, gives the dichloride, b.p. 139°/0.2 mm., which with $d\text{-CHPhMe}\cdot\text{NH}_2$, $[\alpha]_{\text{D}}^{25} + 39.24^\circ$, gives (I). The dl -amine, b.p. 70°/10 mm., is prepared from $\text{CPhMe}\cdot\text{N}\cdot\text{OH}$ by H_2 -Raney Ni in EtOH at 125 atm. in 73% yield.

R. S. C.

Union of aryl nuclei. II. Chloro-, bromo-, and nitro-fluorenones. I. M. HEILBRON, D. H. HEY, and R. WILKINSON (J.C.S., 1938, 113–116).—Ring-closure of nuclear-substituted diphenyl-2-carboxylic acids provides a synthesis of the corresponding substituted fluorenones. Me diphenyl-2-carboxylates are prepared from diazotised $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ (I) (or derivatives) and PhR (or C_6H_5). Use of PhR leads to a mixture of Me 2'- and 4'-substituted-diphenyl-2-carboxylates (cf. A., 1935, 78). Thus diazotised (I) with PhCl and PhBr gives respectively mixtures of Me 2'- and 4'-chloro- and 2'- and 4'-bromo-diphenyl-2-carboxylates; the mixed acids with conc. H_2SO_4 yield respectively mixtures of 4- and 2-chloro- and 4- and 2-bromo-fluorenones. Diazotised (I) gives no product with PhNO_2 . The following are prepared from C_6H_5 and the appropriate $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{R}\cdot\text{CO}_2\text{Me}$: 5-, m.p. 152° (Me ester, b.p. 180–190°/20 mm.), and 4-, m.p. 157°, -chloro-, 5-, m.p. 172° (Me ester, b.p. 185–195°/20 mm.), and 4-, m.p. 164°, -bromo-, and 4-nitro-, m.p. 173°, -diphenyl-2-carboxylic acids, yielding on ring-closure respectively 3-chloro-, m.p. 157°, 2-chloro- (II), m.p. 123°, 3-, m.p. 161°, and 2-, new m.p. 150°, -bromo-, and 2-nitro-, m.p. 219°, -fluorenones. (II) is also obtained by ring-closure of 4'-chlorodiphenyl-2-carboxylic acid, m.p. 161°, prepared by oxidation of 4'-chloro-2-methyldiphenyl, m.p. 288–290° (from diazotised $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ and PhMe).

E. G. B.

Partial synthesis of the methylcyclopentenolone of wood tar. H. GAULT and J. BURKHARD (Compt. rend., 1937, 205, 1416–1417; cf. Meyerfeld, A., 1912, i, 628).—2-Methylcyclopentanone is converted by gaseous Cl_2 or by Cl_2 in CCl_4 into 5:5-dichloro-2-methylcyclopentanone (or, possibly, the 4:5- Cl_2 -isomeride), b.p. 90–95°/13 mm., hydrolysed by boiling H_2O to 3-methylcyclopentane-1:2-dione, m.p. 104° (phenylosazone, m.p. 136°), identical with the methylcyclopentenolone of Rojahn and Rühl.

H. W.

Preparation of benzil from benzoin. E. V. ZMAČINSKI and L. I. MALISHEVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1937, 17, 365–366).—Benzoin yields benzil (90%) and H_2S (96%) when heated with S at 230° for 1½ hr.

A. LI.

Reduction of benzil. I. A. PEARL and W. M. DEHN (J. Amer. Chem. Soc., 1938, 60, 57–59).— Bz_2 [prep. in 90–95% yield from benzoin (I) by $\text{CuSO}_4\text{--NaOH}$] is reduced by KI-red $\text{P}\text{--HCl}$ at 95° to deoxybenzoin (II) (70%) and β -deoxybenzoin pinacone (12%), by $\text{Zn}\text{--Hg}\text{--HCl}$ at 15° to stilbene (85%) and $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{OH}$ (10%), or (I) (90%), by $\text{Sn}\text{--Hg}\text{--HCl}$ at 25° to (I) (96%) or at 75° to (II) (97%), by $\text{Al}\text{--Hg}\text{--HCl}$ or $\text{Al}\text{--Hg}\text{--H}_2\text{O}$ at 25° or by $\text{Mg}\text{--Hg}\text{--HCl}$ at 5° to (I) (90%), by $\text{Al}\text{--HCl}$ at 5° to (I) (90%) and isodidesyl (III) (5%), by $\text{Zn}\text{--NaOH}$ at 100° to didesyl (30%), benzoin pinacone (IV) (10%), and

(III) (6%), by $\text{Zn}\text{--aq. NH}_3$ at 95° to (II) (64%), by $\text{Zn}\text{--NH}_4\text{Cl}$ at 25° to (I) (65–99%), and by $\text{Zn}\text{--H}_3\text{PO}_4$ at 100° to (IV) (10%). $\text{Zn}\text{--NaOH}\text{--EtOH}$ gives 90% of $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$, $\text{Zn}\text{--Hg}\text{--H}_3\text{PO}_4$ at <15° affords stilbene (55%) and isostilbene (35%), whilst $\text{Al}\text{--Hg}\text{--aq. NH}_3$ yields hydrobenzoin (60%). $\text{Al}\text{--NaOH}\text{--EtOH}$, $\text{Zn}\text{--Hg}\text{--aq. NaOH}$, and $\text{Mg}\text{--Hg}\text{--H}_2\text{O}$ are without effect.

R. S. C.

Reactions of maleic and dimethylmaleic anhydride with organo-metallic compounds. D. S. TARBELL (J. Amer. Chem. Soc., 1938, 60, 215–216).—With 4 mols. of MgPhBr maleic anhydride gives $\text{COPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh}$ and a little $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ (I); with 1 mol. of MgPhBr some (I), but no $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ (II), is formed; thus 1:4-addition probably occurs. With the less reactive ZnPhCl , however, 26% of (II) is obtained. Dimethylmaleic anhydride, being also less reactive, with 1 mol. of MgPhBr gives β -benzoyl- α -methylcrotonic acid, dimorphic, m.p. 65–67° and 92–94°, and a little (?) β -benzoyl- α -phenyl- α -methylbutyric acid (III), m.p. 183–185°; with 2 mols. of MgPhBr it gives (III) and a compound, m.p. (? + solvent) 65–68°, 85–94°, or 90–93°, possibly stereoisomeric with (III).

R. S. C.

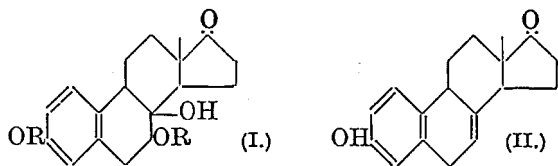
Formation of acetoxy- β -diketones from bromo- α -diketones. A. H. BLATT (J. Washington Acad. Sci., 1938, 28, 1–5).—Replacement of halogen in α -halogenoketones by addition to the CO group followed by $\text{C}\text{>O}$ formation and ring opening (cf. A., 1929, 1072; 1933, 1297; 1937, II, 69) may involve shift of O from CO to an adjacent atom. A halogeno- α -diketone may then give a β -diketone. Thus $\text{COPh}\cdot\text{CO}\cdot\text{CHPhBr}$ (I) with KOAc yields $\text{COPh}\cdot\text{CH}(\text{OAc})\cdot\text{COPh}$ (II) [presumably through $\text{COPh}\cdot\text{C}(\text{OK})(\text{OAc})\cdot\text{CHPhBr}$ and $\text{COPh}\cdot\text{C}(\text{OAc})\text{CHPh}\text{>O}$]. Similarly

$p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CO}\cdot\text{COPh}$ and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{CHPhBr}$ with KOAc both yield α -benzoyl- α - p -anisoylmethyl acetate (III), m.p. 70°. $\text{CHBr}(\text{COPh})_2$, however, gives (II), not $\text{OAc}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{COPh}$, whilst $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHBr}\cdot\text{COPh}$ gives (III), not $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OAc})\cdot\text{CO}\cdot\text{COPh}$ or $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{OAc}$, suggesting that the oxide ring is not formed, but Br directly replaced. With $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$, (I) gives 3-benzoyl-2-phenylquinoxaline, derived from $\text{CO}(\text{COPh})_2$. With HI, there is no change of structure, (I) giving $\text{COPh}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$. With $\text{C}_5\text{H}_5\text{N}$, (I) gives a pyridinium salt, different from that formed by $\text{CHBr}(\text{COPh})_2$, suggesting that the above rearrangements are not due to intermediate formation of $\text{COPh}\cdot\text{CO}\cdot\text{CHPh}^+$.

E. W. W.

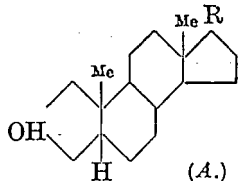
Equilin and its hydrogenation. A. SERINI and W. LOGEMANN [with, in part, HOHLWEG] (Ber., 1938, 71, [B], 186–191).—Addition of OsO_4 to equilin acetate in Et_2O and hydrolysis of the resultant ester gives the sec.-tert.-glycol [(I), $\text{R} = \text{H}$], m.p. 245°, which, with Ac_2O in cold $\text{C}_5\text{H}_5\text{N}$, gives the diacetate [(I), $\text{R} = \text{Ac}$], m.p. 215°, thus confirming the con-

stitution (II) for equilin. Dihydroequilin is not hydrogenated (Raney Ni) in cold MeOH but becomes



disproportionated to dihydroequilenin (III), m.p. 245°, and isoestradiol (IV), $C_{18}H_{24}O_2$, m.p. 181°, $[\alpha]_D^{20} + 18^\circ$ in dioxan. If the temp. of the reaction is raised and the pressure of the H_2 diminished the formation of (III) is facilitated. In the reverse case the production of (III) can be suppressed but even then (IV) is not accompanied by estradiol. (IV), $BzCl$, and cold 5% KOH give the corresponding monobenzoate, m.p. 190°, $[\alpha]_D^{20} + 9.5^\circ$ in dioxan, which is oxidised by CrO_3 in $AcOH$ to isoestrone benzoate, m.p. 196°, $[\alpha]_D^{20} + 61^\circ$ in dioxan, hydrolysed by $n-MeOH-KOH$ to isoestrone, $C_{18}H_{22}O_2$, m.p. 247°, $[\alpha]_D^{20} + 94^\circ$ in dioxan (semicarbazone, m.p. 270°). The oestrogenic activity of the iso-compounds is approx. one third of that of the corresponding estrone compounds, and is roughly that of the equilin derivatives. Introduction of OH into ring II of equilin nullifies the oestrogenic activity. H. W.

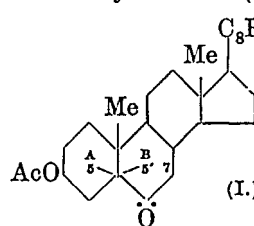
Pregnan-3-ol-20-one. A. BUTENANDT and G. MÜLLER (Ber., 1938, 71, [B], 191—197).—If pregnanediol (I) is hydrogenated (PtO_2) in acid solution ($Et_2O-AcOH$) and the change is interrupted after the absorption of 2 H, the main product is *n*-pregnan-3-ol-20-one (II), m.p. 142—143°, $[\alpha]_D^{20} + 101^\circ$ in $EtOH$ (acetate, m.p. 116.5°, $[\alpha]_D^{20} + 86^\circ$ in $EtOH$; oxime, m.p. 179°); the digitonide, m.p. 199—208°, requires 75% $EtOH$ for its quant. separation. Hydrogenation (Pt -black) of (I) in neutral solution ($Et_2O-EtOH$) gives about 35% of (II) and epipregnan-3-ol-20-one (III), m.p. 148—149°, $[\alpha]_D^{20} + 114^\circ$ in $EtOH$ (acetate, m.p. 99°, $[\alpha]_D^{20} + 123^\circ$ in abs. $EtOH$; oxime, m.p. 224—226°), which does not give a ppt. with digitonin in 75% $EtOH$. (II) is converted by $MgMeI$ in Et_2O into the corresponding carbinol, m.p. 168—171°, $[\alpha]_D^{20} + 16^\circ$ in $EtOH$, which loses H_2O when sublimed at 80°/high vac. and passes into the unsaturated alcohol (A) ($R = \cdot CMe_2$), m.p. 141—142°, $[\alpha]_D^{20} + 15^\circ$ in $EtOH$; this is acetylated, ozonised in $CHCl_3$, and then converted into the acetate of aetiocholan-3-ol-17-one, isolated as the semicarbazone, m.p. 236—238° (the corresponding oxime has m.p. 188—189°). (II) is therefore (A) with $R = Ac$. Similarly, (III) and $MgMeI$ give the corresponding carbinol (as A; $R = \cdot CMe_2 \cdot OH$), m.p. 190—201° (gradual decomp.), $[\alpha]_D^{20} + 22^\circ$ in $EtOH$, which is dehydrated by boiling $AcOH-Ac_2O$ and then hydrolysed to the unsaturated alcohol (as A; $R = \cdot CMe_2$), m.p. 164—165.5°, $[\alpha]_D^{20} + 45^\circ$ in $EtOH$, whence the known acetate of epi-aetiocholan-3-ol-17-one, thus establishing the structure of (III). Reduction of (II) with Na and Pr^oOH gives a *n*-pregnanediol, m.p. 189—190.5°, $[\alpha]_D^{20} + 44^\circ$ in $EtOH$, which does not give a very sparingly sol.



compound with digitonin and is possibly pregnane-3(β)-20(α)-diol (A., 1938, II, 12). The corresponding reduction of (III) leads essentially to the pregnane-diols present in the urine of pregnancy. H. W.

Preparation of epiallopregnan-3-ol-20-one. G. FLEISCHER, B. WHITMAN, and E. SCHWENK (J. Amer. Chem. Soc., 1938, 60, 79).—*allo*-Pregnanedione with H_2-PtO_2 in $HBr-AcOH$ gives *allo*- (acetate, m.p. 144°, $[\alpha]_D^{20} + 79.8^\circ$ in $EtOH$) and *epiallo*-pregnan-3-ol-20-one, m.p. 176—178°, $[\alpha]_D^{20} + 87.7^\circ$ in $EtOH$ (acetate, m.p. 141—142°, $[\alpha]_D^{20} + 94.5^\circ$ in $EtOH$). R. S. C.

Sterol group. XXXIV. Dibromination of 6-ketocholestanyl acetate. I. M. HEILBRON, H. JACKSON, E. R. H. JONES, and F. S. SPRING (J.C.S., 1938, 102—107; cf. A., 1937, II, 344).—6-Ketocholestanyl acetate (I) has been dibrominated with



the object of preparing steroid ketones containing unsaturated centres in rings A and B. (I) (prep. from cholesterol described) with Br (2 mols.) in $Et_2O-AcOH$ at 0° gives the 5- Br -derivative (II) and in $AcOH + a$ little HBr at room temp. (1 hr.), 5:7- (III), m.p. 152°, $[\alpha]_D^{20} - 140^\circ$ in $CHCl_3$, and (18 hr.) 5':7- (IV), m.p. 129°, $[\alpha]_D^{20} - 51.1^\circ$ in $CHCl_3$, -dibromo-6-ketocholestanyl acetates. (II) with Br and HBr (≤ 1 mol. essential) in $AcOH$ gives either (III) or (IV), whilst 7-bromo-6-ketocholestanyl acetate (V) gives only (III). With HBr in $AcOH$, (III) and (IV) revert to (V), so that (III) and (IV) are formed by simultaneous, not consecutive, reactions. Both with boiling C_5H_5N give 6-keto-3-acetoxy- $\Delta^{2:4}$ -cholestadiene, m.p. 139—140°, $[\alpha]_D^{20} + 27^\circ$ in $CHCl_3$ [hydrolysed ($MeOH-NaOMe$) to 3:6-diketo- Δ^4 -cholestene], and 7-hydroxy-6-keto-3-acetoxy- Δ^4 -cholestene, m.p. 227—229° [benzoate, m.p. 136—137°; 3:7-(OH)₂-derivative, m.p. 220—222°]. (II), (III), and (V) do not react with C_5H_5N at room temp., whereas (IV) gives unidentified halogen-free mixtures. Similarly (II), (III), and (V) do not react with $NaOAc$ in $EtOH$, whereas (IV) gives 6:7-diketocholestanyl acetate, 7-bromo-6-keto-3:5'-diacetoxycholestane (VI), m.p. 198° (decomp.), and 6-keto-3-acetoxy-7-ethoxy- Δ^4 -cholestene (VII), m.p. 119—120°. (VI) is also obtained as sole product from (IV) and $KOAc$ in $EtOH$, and with $Al-Hg$ in moist Et_2O gives 6-keto-3:5'-diacetoxycholestane, m.p. 169—170°, hydrolysed to the corresponding 3:5'-(OH)₂-compound, m.p. 232°, different from the 3:5-dihydroxy-6-ketocholestane, m.p. 138°, obtained by hydrolysis of (II). (VII) with cold $KOH-EtOH$ or hot $MeOH-NaOMe$ gives 3-hydroxy-6-keto-7-ethoxy- Δ^4 -cholestene, m.p. 113°. (IV) with $KOAc$ in $BuOH$ gives 6-keto-7-methoxy- $\Delta^{2:4}$ -7-cholesta-triene, m.p. 119—121°. E. G. B.

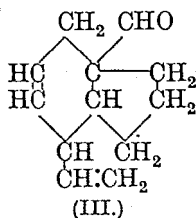
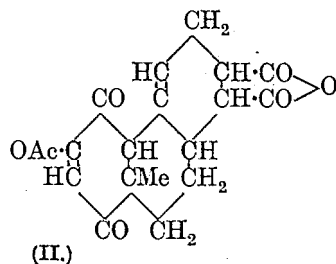
Biochemical dehydrogenation in the series of the testicular hormone. Genesis of sex hormones. A. VERCELLONE and L. MAMOLI (Ber., 1938, 71, [B], 152—154).—Both OH groups of androstene-3:17-diol become oxidised when it is shaken with O_2 in presence of impoverished yeast and PO_4 buffer at 32°; Δ^4 -androstene-3:17-dione is formed. H. W.

Biochemical transformation of dehydroandrosterone into androstenedione. Genesis of the testicular hormone. L. MAMOLI and A. VERCELLONE (Ber., 1938, 71, [B], 154—156).—Dehydroandrosterone (I) is smoothly dehydrogenated to Δ^4 -androstenedione by impoverished yeast in an atm. of O_2 , the yield being 70%. (I) is biochemically converted into Δ^4 -testosterone in about 53—55% yield, which greatly exceeds that obtained with chemical reagents. Displacement of the double linking in androstenediol occurs during biochemical dehydrogenation. H. W.

Transformation of Δ^4 -androstenedione into ætiocholane-3:17-dione by an enzymic extract of the testes of the stallion. A. ERCOLI and L. MAMOLI (Ber., 1938, 71, [B], 156—158).—Finely divided Δ^4 -androstenedione (I) is added to an aq. extract of the testes of the stallion; after 20 days at 37° *ætiocholane-3:17-dione*, m.p. 131—132°, $[\alpha]_D^{25} +113^\circ$ in EtOH, is isolated. Its constitution is established by its bromination in AcOH containing HBr to 4-bromo*ætiocholane-3:17-dione*, m.p. 195° (decomp.), which passes in boiling C_5H_5N into (I). H. W.

Increased activity of male sexual hormone on esterification. K. MIESCHER *et al.* (Biochem. Z., 1937, 294, 39—60).—See A., 1938, III, 194. The following are described. *Androsterone n-butyrate*, m.p. 102—103°; *androsterone-3-cis-17-trans-diol 3-propionate*, m.p. 120—121°, *3-n-butyrate*, m.p. 124—125°, *3-palmitate*, m.p. about 40°, *3:17-dipropionate*, m.p. 121.5—122.5°; *dihydrotestosterone formate*, m.p. 141—142.5°, *propionate*, m.p. 121—121.7°, *n-butyrate*, *forms*, m.p. 90.5—91° and 100—101°, and *n-valerate*, m.p. 102.5—103°; *testosterone chloroformate*, m.p. 139—140.5°; *testosterone Me*, m.p. 140.5—141.5°, *Et*, m.p. 141—142°, *Pr^a*, m.p. 87—89°, *Bu^a*, an oil, *Ph*, m.p. 144.5—145.5°, *CH₂Ph*, m.p. 156.5—157°, and β -diethylaminoethyl carbonate, hydrochloride +0.5H₂O, m.p. 178—180°; *testosterone carbamate*, +0.5H₂O, m.p. 155—157°, *N-n-propylcarbamate*, m.p. 190—191°, *chloroacetate*, m.p. 123—124°, α -bromopropionate, m.p. 187—188°, α -dimethylaminopropionate, m.p. 83—85°, *phenylacetate*, m.p. 129—131° (corr.), and *crotonate*, m.p. about 158—159°.

Diene synthesis of polycyclic compounds, with or without angular substituents, from hexatriene. L. W. BUTZ (J. Amer. Chem. Soc., 1938, 60, 216—217).— $\Delta^{\alpha\alpha\epsilon}$ -Hexatriene (I) and 4-acetoxy-*p*-tolu-2:5-quinone in EtOH at 90—95° give 2-acetoxy-10-methyl-8-vinyl-5:8:9:10-tetrahydro-



naphtha-1:4-quinone, m.p. 192—195° after decomp. at 161—162°; the remainder of the reaction product

with maleic anhydride in C_6H_6 at 150—160° gives 25% of the substance (II), decomp. 225°. (I) and cyclopenten-1-al in EtOH at 90—95° give the aldehyde (III) (*semicarbazone*, m.p. 173—175°). R. S. C.

3-Benzamido-1:2-naphthaquinone. H. GOLDSTEIN and G. GENTON (Helv. Chim. Acta, 1938, 21, 56—61).—3:2-NH₂·C₁₀H₆·OH with Bz₂O and NaOAc in AcOH at 80° gives 3-benzamido-2-naphthol (I), m.p. 235°, in 70% yield. Addition of 2N-H₂SO₄ to a solution of (I) in NaOH and NaNO₂ at 0° gives 1-nitroso-3-benzamido-2-naphthol (II), m.p. 202° (decomp.), which gives characteristically coloured lakes with FeSO₄, FeCl₃, CoCl₂, and CuSO₄. This is reduced by SnCl₂ and cone. HCl to 1-amino-3-benzamido-2-naphthol [*hydrochloride* (III); 1:3-dibenzamido-2-naphthol, m.p. 254°]. Oxidation of (III) with FeCl₃ in HCl affords 3-benzamido-1:2-naphthaquinone (IV), m.p. 199° (decomp.), the *oxime* of which is identical with (II). (IV) and *o*-C₆H₄(NH₂)₂·HCl yield 4-benzamido-1:2-benzophenazine, m.p. 220°. H at C₁₀ in (IV) is so mobile that (IV) is converted by HCl in AcOH into 4-chloro-3-benzamido-1:2-dihydroxynaphthalene, m.p. 160° (decomp.), oxidised by FeCl₃ to 4-chloro-3-benzamido-1:2-naphthaquinone, m.p. 175° (decomp.), whence 3-chloro-4-benzamido-1:2-benzophenazine, m.p. 276°. Passage of air through a solution of (IV) and NH₂Ph in EtOH at 70° gives 3-benzamido-4-anilino-1:2-naphthaquinone, m.p. 296—297°, converted by boiling glacial AcOH into 1:2-diphenyl- α -naphthiminazole-4:5-quinone, m.p. 312°, which with *o*-C₆H₄(NH₂)₂ affords the corresponding phenazine, m.p. 295°. M.p. are corr. H. W.

Method of ring-closure of 2-carboxydiaryl ketones. H. WALDMANN (J. pr. Chem., 1938, [ii], 150, 121—123).—Good yields of anthraquinones from *o*-CO₂H·C₆H₄·COAr by means of BzCl usually depend on the presence of acidic impurities, and addition of H₂SO₄ to the pure compounds often increases the yield. *o*-C₆H₄(CO)₂O with (not without) a few drops of H₂SO₄ is an excellent reagent for ring-closure; examples are *o*-CO₂H·C₆H₄·COPh, 1-C₁₀H₇·CO·C₆H₄·CO₂H-*o*, 1:2-C₁₀H₆Cl·CO·C₆H₄·CO₂H-*o*, 2:3-C₁₀H₆Bz·CO₂H, 8-benzoyl-fluorene- and -fluorenone-1-carboxylic acid. R. S. C.

lin-Benzanthraquinones. H. WALDMANN and G. POLAK (J. pr. Chem., 1938, [ii], 150, 113—120).—*o*-1'-Chloro-2'-naphthoylbenzoic acid, m.p. 168—169° (*Me* ester, m.p. 101°), with P₂O₅ in PhNO₂ at 180° (or less satisfactorily) conc. H₂SO₄ at 130—135°, or its acid chloride (prep. from the 1'-OH-acid and PCl₅) alone or in PhNO₂ at about 210°, gives 1-chloro-2:3-benzanthraquinone, yellow, m.p. 261°, converted by NH₂Bz, CuCl₂, and NaOAc in PhNO₂ at 180° into the yellow vat dye, 1-benzamido-2:3-benzanthraquinone, m.p. 298°, by *p*-C₆H₄Me·SO₂·NH₂, K₂CO₃, and Cu(OAc)₂ in PhNO₂ at 210° into the 1-*p*-toluenesulphonamido-quinone (I), m.p. 231°, by NH₂Ph or *p*-C₆H₄Me·NH₂ and anhyd. NaOAc at 170—180° into the 1-anilino-, m.p. 244°, or 1-*p*-toluidino-quinone, m.p. 216°, respectively, and by Cu in PhNO₂ at 220—230° into 2:3:2':3'-dibenz-1:1'-dianthraquinonyl, m.p. >350° (with Cu and cold H₂SO₄ gives 2:3:2':3'-dibenzhelianthrone, m.p. >350°). With *p*-

$C_6H_4Me \cdot SO_3Me$ and K_2CO_3 in $C_6H_4Cl_2$ at 170—180° (I) gives 1-methylamino-2:3-benzanthraquinone, m.p. 209° (by way of the $p\text{-}C_6H_4Me \cdot SO_3\cdot$ derivative, m.p. 228.5°), and with conc. H_2SO_4 affords 1-amino-2:3-benzanthraquinone, m.p. 266° [Bentley's compound (J.C.S., 1907, 91, 415), m.p. 290—292°, is impure], which affords (diazo-reaction) 1-bromo-2:3-benzanthraquinone, m.p. 235.5°. R. S. C.

Synthesis of hystazarin. H. WALDMANN (J. pr. Chem., 1938, [ii], 150, 99—106).—Gradual addition of $o\text{-}C_6H_4(CO)_2O$ and $o\text{-}C_6H_4(OH)_2$ to $AlCl_3\text{--}NaCl$ at 110° and heating to 130—138° gives 3:4-dihydroxybenzophenone-2'-carboxylic acid, m.p. 207° (Me ester, m.p. 178°), converted by conc. H_2SO_4 at 100° into hystazarin (90%; diacetate, m.p. 210°; dibenzoate, m.p. 236°; di-*p*-toluenesulphonate, m.p. 204°) and alizarin (10%), separated by sublimation. 3:1:2- $C_6H_3Cl(CO)_2O$ gives similarly 3'-(or 6'-)chloro-3:4-dihydroxybenzophenone-2'-carboxylic acid, m.p. 187°, and thence 5-chlorohystazarin (90%), m.p. >300° (diacetate, m.p. 193°), and 5-(or 8-)chloroalizarin. 4:1:2- $C_6H_3Cl(CO)_2O$ gives 4'-(or 5'-)chloro-3:4-dihydroxybenzophenone-2'-carboxylic acid, m.p. 234°, and thence 6-chlorohystazarin, m.p. >310° (diacetate, m.p. 204.5°), and 6-(or 7-)chloroalizarin. 3:6:1:2- $C_6H_2Cl_2(CO)_2O$ gives 3':6'-dichloro-3:4-dihydroxybenzophenone-2'-carboxylic acid, m.p. 205—206°, and thence about equal amounts of 5:8-dichloro-hystazarin (diacetate, m.p. 217°) and -alizarin, m.p. 257° (diacetate, m.p. 178°). R. S. C.

Nitration of hystazarin. H. WALDMANN and E. WIDER (J. pr. Chem., 1938, [ii], 150, 107—112).—Hystazarin with 1 or 2 mols. of KNO_3 in H_2SO_4 gives the 1- $NO_2\cdot$, m.p. 244°, or 1:4-(NO_2)₂-derivative, m.p. 224°, respectively. The Me_2 ether affords 1-nitro-2:3-dimethoxyanthraquinone, m.p. 233°. Reduction ($Na_2S_2O_4$) gives 1-amino- and 1:4-diamino-hystazarin, both m.p. >316°, and 1-amino-2:3-dimethoxyanthraquinone, m.p. 171.5°. The diamine with an excess of $PhCHO$ and a little piperidine at 150° gives the bisdiphenyloxazole, m.p. >310°. $o\text{-}C_6H_4Cl \cdot OH$ and $o\text{-}C_6H_4(CO)_2O$ added to $AlCl_3\text{--}NaCl$ at 130—150° give 3-chloro-4-hydroxybenzophenone-2'-carboxylic acid, m.p. 219°, converted by H_2SO_4 into 3-chloro-2-hydroxyanthraquinone, m.p. 266°, which gives the 1- $NO_2\cdot$, m.p. 239°, and 1- $NH_2\cdot$ -derivative, m.p. 231° (gives the phenyloxazole, m.p. >310°). R. S. C.

New product of the reaction between anthraquinone and alkali. N. N. VOROSCHCOV, A. P. ALEXANDROV, and T. I. BERKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1937, 17, 361—363).—Aq. $NaOH$, Na_2SO_3 , and anthraquinone in an autoclave at 210° (5—6 hr.) yield anthraquinol (44%), ahzarin (2%), and 2:10-dihydroxy-9-keto-2:9-dihydroanthracene (I) (31%), m.p. 303—306° (decomp.). (I) heated alone yields 2-hydroxyanthraquinone but in benzenoid solvents gives dianthrone (identified by reduction and acetylation or methylation). (I) with $Ac_2O + NaOH$ gives dianthrone and 2-acetoxyanthraquinone. A. Li.

Catalytic reduction and hydrogenation of hydroxyanthraquinones. K. ZAHN and H. KOCH

(Ber., 1938, 71, [B], 172—186).—Catalytic hydrogenation at >170°/20—80 atm. of 1-hydroxyanthraquinone (I) with a relatively small proportion of Ni-kieselguhr in $PhCl$ gives exclusively 1-hydroxy-9-anthrone (II), m.p. 140—141° [whence 1:9-diacetoxyanthracene, m.p. 210—211° (lit. 148—149°)]. It appears that 1-hydroxyanthraquinol first results and this becomes transformed into 1-hydroxy-9:10-dihydroanthraquinol which spontaneously suffers transannular loss of H_2O with formation of (II). Under similar conditions alizarin, chrysazin, and 1-hydroxy-4-methylanthraquinone afford respectively 1:2-dihydroxy-, m.p. 148—150°, 1:8-dihydroxy-, m.p. 177—179°, and 1-hydroxy-4-methyl-, m.p. 167—168°, -9-anthrone. 4-Hydroxy-1-methyl-9-anthrone, m.p. 223—225°, is obtained by reducing 1-acetoxy-4-methylanthraquinone with $Na_2S_2O_4$ at 65°. In all cases O vicinal to an $\alpha\text{-}OH$ is retained in the mol. Similar treatment of the corresponding ethers gives alkoxyanthrones with loss of O in *peri* position to $\alpha\text{-}OAlk$. Thus 1-methoxyanthraquinone in $PhCl$ affords 4-methoxy-9-anthrone, m.p. 142—143°, whence 9-acetoxy-4-methoxyanthracene, m.p. 130—132°. Alizarin Me_2 ether gives 3:4-dimethoxy-9-anthrone, m.p. 148—156°, and 4:5-dimethoxy-9-anthrone, m.p. 234—236° (Ac derivative, m.p. 216°), is obtained from chrysazin Me_2 ether. Quinizarin Me_2 ether (III) yields 1:4-dimethoxy-9-anthrone, m.p. 140—141° (whence 9-acetoxy-1:4-dimethoxyanthracene, m.p. 125—126°), also obtained by action of conc. H_2SO_4 at 15° on 2:5-dimethoxydiphenylmethane-2'-carboxylic acid, and transformed by $FeCl_3$ in hot $AcOH$ into tetramethoxydianthrone, m.p. 248°. Catalytic hydrogenation of (I) in $PhCl$ at 80—120°/70—50 atm. in presence of a larger proportion of Ni leads to 9:10-dihydroxy-1-keto-1:2:3:4-tetrahydroanthracene (IV), m.p. 170—171°, dehydrogenated to (I) when its alkaline solution is exposed to air. When cautiously treated with Ac_2O and $KOAc$ at 60° it gives 9-hydroxy-1-keto-10-acetoxy- (V), m.p. 149—150°, and when more drastically treated it affords 1-keto-9:10-diacetoxy- (VI), m.p. 215—216°, -1:2:3:4-tetrahydroanthracene. Under extreme conditions 1:9:10-triacetoxy-3:4-dihydroanthracene (VII), m.p. 169—170°, results; its constitution follows from its alkaline hydrolysis and dehydrogenation to (I) and from the quantitative formation of a dibromide, decomp. 248—250°. Methylation of (IV) by cold $NaOH$ and Me_2SO_4 affords 9-hydroxy-1-keto-10-methoxy-, m.p. 94° (acetate, m.p. 128—129°), whereas $p\text{-}C_6H_4Me \cdot SO_3Me$ and Na_2CO_3 in $PhCl$ give 1-keto-9:10-dimethoxy-, m.p. 116—117°, -1:2:3:4-tetrahydroanthracene. Oxidation of (IV) with $Pb(OAc)_4$ in $AcOH$ gives 1-keto-1:2:3:4-tetrahydroanthraquinone, m.p. 148—150°, isomerised when cautiously warmed in HCl containing C_5H_5N to 1-hydroxy-2:3-dihydroanthraquinone, which blackens when heated but melts if brought into a bath at 200°. 1:1-Diacetoxy-1:2:3:4-tetrahydroanthraquinone has m.p. 175—176°. (V) and $NHPh \cdot NH_2$ in boiling $EtOH$ give the 1-phenylhydrazine, decomp. 234°, also obtained from (VI) or (VII), converted by alkaline hydrolysis in presence of air into 1-benzeneazanthraquinone, m.p. 164°, reduced ($Na_2S_2O_4$) to 1-aminoanthraquinone. (IV) and NH_2Et in boiling aq. $EtOH$ give 1-

ethylimino-9:10-dihydroxy-1:2:3:4-tetrahydroanthracene, m.p. 198—199° (10-*Ac* derivative, m.p. 159—160°) (converted by alkali and air into 1-*ethylaminoanthraquinone*, m.p. 124—125°), transformed by prolonged treatment with $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ into 1-*acetethylamido-9:10-diacetoxy-3:4-dihydroanthracene*, m.p. 218—220°, which is similarly hydrolysed to 1-*acetethylamidoanthraquinone*, m.p. 153—154°. (IV), $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, and H_3BO_3 at 130—140° give a product, m.p. 290° (red at 200°), dehydrogenated in 50% MeOH containing a little alkali to 1-*p-toluidinoanthraquinone*, m.p. 156—157°. Exhaustive hydrogenation of (IV) at 120—130°/80—60 atm. in BuOH containing Ni leads to 9:10-dihydroxy-1-keto-1:2:3:4:5:6:7:8-octahydroanthracene (VIII), m.p. 236—237° (*Ac*, m.p. 140°, and *Ac*₂, m.p. 215—216°, derivatives; *phenylhydrazone*, m.p. 181—183°), oxidised by $\text{Pb}(\text{OAc})_4$ in AcOH to 1-keto-1:2:3:4:5:6:7:8-octahydroanthraquinone, m.p. 150—152°. (II) is reduced [Ni in BuOH at 120—130° or red P and boiling HI (*d* 1.9)] to 9-hydroxy-1-keto-1:2:3:4-tetrahydroanthracene, m.p. 99° (*Br*₁-derivative, m.p. 138—139°), whence 1:9-diacetoxy-3:4-dihydroanthracene, m.p. 189—190°. Exhaustive hydrogenation of (II) in BuOH at 120—130°/70—50 atm. leads to a mixture of 1:2:3:4:5:6:7:8-octahydroanthranol (*Bz* derivative, m.p. 127—128°) and its 1-keto-derivative (*phenylhydrazone*, m.p. 174—175°). Hydrogenation of quinizarin and its diacyl derivatives without loss of O has not been found possible. Treatment of (III) in PhCl with Ni and H_2 at 80—120°/60—40 atm. gives 1:4-dimethoxy-2:3:5:6:7:8-hexahydroanthraquinone (IX), m.p. 156°, whence 9:10-diacetoxy-1:4-dimethoxy-5:6:7:8-tetrahydroanthracene, m.p. 220—222°. 1:4-Diethoxy-2:3:5:6:7:8-hexahydroanthraquinone, m.p. 142—143°, similarly prepared, yields 9:10-diacetoxy-1:4-diethoxy-5:6:7:8-tetrahydroanthracene, m.p. 187—188°. Dehydrogenation of (IX) by FeCl_3 in hot AcOH gives 1:4-dimethoxy-5:6:7:8-tetrahydroanthraquinone, m.p. 153°; the corresponding diethoxy-compound has m.p. 129—131°. Hydrolysis of (IX) with H_2SO_4 affords 9:10-dihydroxy-1:4-diketo-1:2:3:4:5:6:7:8-octahydroanthracene (X), m.p. 169—170° (1:4-bisphenylhydrazone, m.p. 235°), oxidised by $\text{Pb}(\text{OAc})_4$ in AcOH to 1:4-diketo-1:2:3:4:5:6:7:8-octahydroanthraquinone, m.p. (indef.) 155° [whence diacetyl-5:6:7:8-tetrahydroquinizarin (XI), m.p. 205—206°]. Enolising acetylation of (X) gives 1:4:9:10-tetraacetoxy-5:6:7:8-tetrahydroanthracene, m.p. 222—223°, also obtained from (XI) by reduction ($\text{Na}_2\text{S}_2\text{O}_4$, dil. AcOH) and subsequent acetylation. H. W.

Substituted anthraquinones.—See B., 1938, 140.

β -Phellandrene. A. K. MACBETH, G. E. SMITH, and T. F. WEST (J.C.S., 1938, 119—123).—The α -nitrosite (I) of *l*- β -phellandrene from Canada balsam has m.p. 101—102°, $[\alpha]_D^{20} +165.3^\circ$ in CHCl_3 , and the α -nitrosite (II) of *d*- β -phellandrene from water-fennel oil has m.p. 102—103°, $[\alpha]_D^{20} -165.7^\circ$ in CHCl_3 ; these vals. are very close to those of α -phellandrene derivatives. The mutarotation of β -phellandrene α -nitrosite proceeds slowly and $[\alpha]$ does not fall to half the initial val. With NaOH, the nitrosite gives nitrophellandrene, reduced to cuminal; (I) yields a nitrophellandrene, $[\alpha]_D^{20} -78.8^\circ$, and (II) affords the compound, $[\alpha]_D^{20} +107.5^\circ$ in EtOH. Oxidation of (I) and (II) leads, according to conditions, to phellandrol or 4-isopropyl- Δ^2 -cyclohexene-1-one. The absorption spectrum of β -phellandrene in C_6H_{12} shows a max. at 2312 Å. with $\log \epsilon$ 3.96. F. R. S.

Catalytic oxidation of camphene. B. N. RUTOVSKI and A. D. BELOGOLOV (Prom. Org. Chim., 1937, 4, 673—676).—Camphene (I)—air-steam mixtures are passed over a $\text{Cr}_2\text{O}_3\text{-SnO}_2$ catalyst at 150° and 350°. The (I) is recovered unchanged, except for about 5% oxidised to CO_2 . Identical results were obtained in presence of AcOH, or with bornyl acetate in place of (I). Borneol or isoborneol gives camphor, in 71 and 48% yield, respectively. R. T.

Dialkyl- α -camphoramic acids. P. GOISSEDET and R. DESPOIS (Compt. rend., 1937, 205, 1239—1241).—Me *cis-d*-camphorate with NH_4Et_2 at 190—200° under pressure affords a neutral product, camphoric acid, and diethyl- α - and - β -camphoramic acid. *d-cis*-Camphoryl chloride (1 mol.) with NHMe_2 (4 mols.) in C_6H_6 at 5° affords dimethyl- α -*d-cis*-camphoramdimethylamide, m.p. 91°. The following are prepared similarly: methylethyl- α -*d-cis*-camphoramethylethyl-, m.p. 61°, diethyl- α -*d-cis*-camphoramdiethyl-, m.p. 130° (also from *l-cis*-camphoryl chloride), dibutyl- α -*d-cis*-camphoramdibutyl-, b.p. 222°/1 mm., and diisomyl- α -*d-cis*-camphoramdiisomyl-, b.p. 232°/1.5 mm., and diethyl-*l-trans*-camphoramdiethyl-amide, m.p. 80°. Dialkyl- α -camphoramic acids (cf. A., 1908, i, 860) with SOCl_2 afford acid chlorides which react with primary and secondary amines to give the tetra-alkyldiamides. The following are prepared: methylethyl- α -*d-cis*-camphoram-dimethyl-, m.p. 74°, and -diethyl-, b.p. 182°/2 mm., dimethyl- α -*d-cis*-camphoram-methylethyl-, m.p. 54—55°, and -diethyl-, m.p. 41—42°, diethyl- α -*d-cis*-camphoram-dimethyl-, m.p. 56°, -methylethyl-, m.p. 86°, -methyl-, m.p. 117°, and -ethylamide, b.p. 185°/2.5 mm. J. L. D.

Bornyl esters of oxalic and tartaric acid. E. B. ABBOT, A. MCKENZIE, and J. O. McB. ROSS (Ber., 1938, 71, [B], 16—27).—Treatment of anhyd. $\text{H}_2\text{C}_2\text{O}_4$ with (–)-borneol (I) and HCl at 100° gives di-(–)-bornyl oxalate (II), m.p. 106.5°, $[\alpha]_D^{20} -59.1^\circ$ in CHCl_3 , also obtained from (I) and $(\text{COCl})_2$ in $\text{C}_5\text{H}_5\text{N}$ at room temp. Di-(+)-bornyl oxalate (III), obtained similarly by the esterification method, has m.p. 106.5°, $[\alpha]_D^{20} +58.8^\circ$ in CHCl_3 . When mixed with an equal wt. of (II) it gives di-dl-bornyl oxalate (IV), m.p. 107.5°, also obtained from $\text{H}_2\text{C}_2\text{O}_4$ and dl-borneol in presence of HCl. This is shown by Roozeboom's method not to be a dl-conglomerate. All mixtures of (II) and (III) melt sharply at the same temp. so that an unbroken series of mixed crystals exists. As by-product of the prep. of (II) a liquid, sol. in alkali, is obtained which sooner or later solidifies and then consists of a mixture of (II) and $\text{H}_2\text{C}_2\text{O}_4$. Partial hydrolysis of (II) also gives a liquid which, when distilled under diminished pressure, affords CO_2 and (–)-bornyl formate, b.p. 65—67° 1 mm., $[\alpha]_{546}^{20} -54.1^\circ$ in EtOH. The isolation of (+)-bornyl (–)-bornyl oxalate could not be achieved. Treatment of the freshly prepared liquid derived from the

semi-hydrolysis of (III) with (I) yielded (IV) as sole isolable product.

(+)-Tartaric acid is converted by (+)-borneol and HCl into *di*-(+)-*bornyl* (+)-*tartrate* (V), m.p. 117.5–118.5°, $[\alpha]_D^{25} + 71.4^\circ$, $[\alpha]_{5461}^{20} + 81.8^\circ$ in CHCl_3 . *Di*-(+)-*bornyl* (+)-*tartrate* (VI) has m.p. 132.5–133.5°, $[\alpha]_D^{25} - 6.2^\circ$ in COMe_2 , $[\alpha]_{5461}^{20} - 8.1^\circ$ in CHCl_3 . A mixture of (V) and (VI) in equal amounts in COMe_2 and removal of the solvent gives a residue with m.p. 95–105°, $[\alpha]_{5461}^{20} + 36.5^\circ$ in CHCl_3 ; it gives homogeneous (VI) when repeatedly cryst. from aq. EtOH and is regarded provisionally as *di*-dl-*bornyl* (+)-*tartrate*. The m.p. curve of mixtures of (V) and (VI) is generally of the conglomerate type but mixtures with 30–45% of (VI) melt sharply at 100° and show that the components form mixed crystals within these limits. Partial hydrolysis of the requisite esters affords (+)-*bornyl* *H* (+)-*tartrate* (VII), m.p. 130.5–131.5°, $[\alpha]_D^{25} + 51.8^\circ$, $[\alpha]_{5461}^{20} + 58.9^\circ$ in EtOH, and (–)-*bornyl* *H* (+)-*tartrate* (VIII), m.p. 157.5–158.5°, $[\alpha]_D^{25} - 6.5^\circ$, $[\alpha]_{5461}^{20} - 8.3^\circ$ in EtOH. Equal quantities of (VII) and (VIII) yield dl-*bornyl* *H* (+)-*tartrate*, m.p. 140–145°, $[\alpha]_{5461}^{20} + 25.3^\circ$ in EtOH, which is partly resolved by a single crystallisation from CHCl_3 . The diastereoisomeric esters form a continuous series of mixed crystals. The action of (+)-borneol on (VIII) leads to a mixture of esters, m.p. 90–100°, $[\alpha]_{5461}^{20} + 46.2^\circ$ in CHCl_3 , which crystallises unchanged from aq. EtOH. Small amounts of (VI) are isolated from the products of the interaction of (I) with (VII). (+)-Diacetyltartaric anhydride and (I) at 100° afford the glassy (–)-*bornyl* *H* (+)-*diacetyltartrate*, $[\alpha]_D^{25} - 12.3^\circ$, $[\alpha]_{5461}^{20} - 15.1^\circ$ in EtOH. H. W.

Menthyl and bornyl malonate. E. B. ABBOT, E. W. CHRISTIE, and A. MCKENZIE (Ber., 1938, 71, [B], 9–15; cf. A., 1934, 777).—Esterification of $\text{CH}_2(\text{CO}_2\text{H})_2$ by (+)-menthol at 100° gives *di*-(+)-*menthyl* malonate (I), m.p. 59–60°, $[\alpha]_D^{20} + 80.2^\circ$ in CHCl_3 , transformed by partial hydrolysis into (+)-*menthyl* *H* malonate, m.p. 57–58°, $[\alpha]_D^{25} + 70.6^\circ$ in CHCl_3 . Equal wts. of (I) and *di*-(–)-*menthyl* malonate in COMe_2 afford, after removal of the solvent, *r*-*dimenthyl* malonate, m.p. 54.5–55.5°, also obtained by esterifying $\text{CH}_2(\text{CO}_2\text{H})_2$ with dl-menthol, but (+)-*menthyl* (–)-*menthyl* malonate could not be obtained. Esterification of $\text{CH}_2(\text{CO}_2\text{H})_2$ by (–)-borneol and HCl at 100° yields dl-(–)-*bornyl* malonate (II), b.p. 219–220°/6 mm., m.p. 31°, $[\alpha]_D^{20} - 41.9^\circ$, $[\alpha]_{5461}^{20} - 49.6^\circ$ in COMe_2 , and (–)-*bornyl* *H* malonate (III), m.p. 65–66°, $[\alpha]_D^{20} - 36.8^\circ$, $[\alpha]_{5461}^{20} - 43.3^\circ$ in CHCl_3 , also obtained by partial hydrolysis of (II). *Di*-(+)-*bornyl* malonate (IV), b.p. 217–218°/6 mm., $[\alpha]_D^{20} + 41.3^\circ$, $[\alpha]_{5461}^{20} + 49.3^\circ$ in COMe_2 , and (+)-*bornyl* *H* malonate (V), m.p. 65–66°, $[\alpha]_D^{20} + 36.2^\circ$, $[\alpha]_{5461}^{20} + 43.2^\circ$ in CHCl_3 , are described. Equal amounts of (II) and (IV) lead to *r*-*di*bornyl malonate, b.p. 217–218°/6 mm., which after being seeded with (II) solidifies to a form, m.p. 36°, which passes into a second variety, m.p. 46°, when cryst. from aq. MeOH. Equal amounts of (III) and (IV) give dl-*bornyl* *H* malonate, m.p. 70–71°. The m.p. curve shows the existence of a continuous series of mixed crystals which exhibits a temp. max. at equimol. concns. of the components. The formation of a true racemic compound is not,

however, completely excluded by such a graph since a racemate can give mixed crystals with each antimeride. Treatment of (III) with *d*-borneol or of (V) with *l*-borneol in absence of a catalyst gives a normal ester of m.p. about 51–53°, so that (+)-*bornyl* (–)-*bornyl* malonate appears to have been produced, but the products are invariably optically active so that in consequence of the formation of mixed crystals it appears impossible to obtain the product completely free from isomerides. The product of the action of dl-borneol on $\text{CH}_2(\text{CO}_2\text{H})_2$ in presence of HCl or on $\text{CH}_2(\text{COCl})_2$ is a mixture, b.p. 219–221°/6 mm., m.p. 40–44°, which could not be separated into its components. The asymmetric synthesis of $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ is effected by condensing (–)-menthyl *H* malonate with PhCHO in $\text{C}_5\text{H}_5\text{N}$ followed by hydrolysis; the crude material has $[\alpha]_D^{25} - 4^\circ$ in EtOH and contains $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, whilst $[\alpha]_D - 18.9^\circ$ is recorded for the homogeneous acid.

H. W.

Constitution of caryophyllene. H. N. RYDON (Chem. and Ind., 1938, 123–125).—Two alternative formulæ are suggested and used for discussing the behaviour of caryophyllene: $\text{CR}_2\cdot\text{CH}\cdot\text{CH}_2\text{---CMe}\cdot\text{CH}$ $\text{CR}_2\cdot\text{CH}\cdot\text{CH}(\text{CMe}\cdot\text{CH}_2)\cdot\text{CH}_2$ with $\text{R} = \text{Me}$, $\text{R}' = \text{H}$, or $\text{R} = \text{H}$, $\text{R}' = \text{Me}$.

F. R. S.

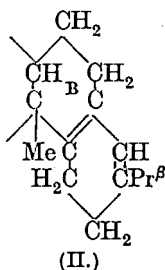
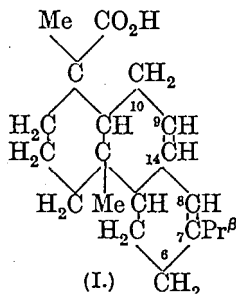
Architecture of the polyterpenes. L. RUZICKA (Angew. Chem., 1938, 51, 5–11).—A review of the development of the knowledge of sesquiterpenes, diterpenes, pentacyclic triterpenes, and of biologically important natural products of unknown constitution due to the adoption of the isoprene hypothesis and application of new methods of dehydrogenation.

H. W.

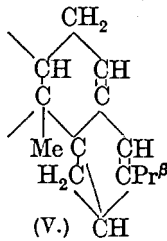
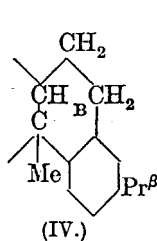
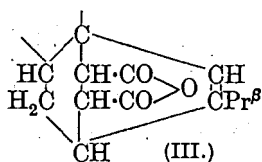
Synthesis of polyterpenoid compounds. IV. J. W. COOK and C. A. LAWRENCE (J.C.S., 1938, 58–63).—4-Methoxycyclohexanone, $\text{Et}_2\text{C}_2\text{O}_4$, and Na give *Et* 4-methoxycyclohexanone-2-glyoxylate, b.p. 116°/0.4 mm. [Cu^{II} compound, m.p. 161–163° (decomp.)]; *bis*-2 : 4-dinitrophenylhydrazones, m.p. 224–227° (decomp.), which when heated affords *Et* 4-methoxycyclohexanone-2-carboxylate, b.p. 131–133°/10 mm. [2 : 4-dinitrophenylhydrazones, m.p. 129–131° (decomp.)], in 25% yield. This keto-compound (Na derivative) and γ -iodobutyronitrile afford *Et* 4-methoxy-2- γ -cyanopropylcyclohexanone-2-carboxylate, b.p. 155°/0.2 mm. (2 : 4-dinitrophenylhydrazones, m.p. 123–126°), hydrolysed to γ -(2-keto-5-methoxycyclohexyl)butyric acid (I), b.p. about 185°/1 mm. (semicarbazone, m.p. 178–178.5°), in 25% yield, and the anhydride of a γ -2-ketocyclohexenylbutyric acid, b.p. 251–260°/0.4 mm. This anhydride is hydrolysed to an acid (semicarbazone, m.p. 219–220.5°) and isomerised by $\text{Ba}(\text{OH})_2$ to an acid [semicarbazone, m.p. 213.5–215° (decomp.)]. The ester of (I) and MgMeI give γ -(5-methoxy-2-methyl- Δ^1 -cyclohexenyl)butyric acid, cyclised with loss of MeOH to 1-keto-9-methylhexahydronaphthalene (?), b.p. 150°/30 mm. [2 : 4-dinitrophenylhydrazones, m.p. 224° (decomp.); semicarbazone, m.p. 214–216° (decomp.)], and not the required 6-OMe-compound.

1-Ethynylcyclohexanol (*p*-nitrobenzoate, m.p. 64–64.5°; 3 : 5-dinitrobenzoate, m.p. 104.5–106°) is reduced (Pd-H_2) to 1-vinylcyclohexanol, b.p. 67–68°/

with sterol derivatives the absorption max. at 2725 Å. and the abnormal reaction with maleic anhydride indicate that the ethylenic linkings are in different rings. Positions 9:10 and 8:14 are excluded by the failure of (I) to lactonise. Position 7:8 is indicated by isolation of $\text{Pr}^{\beta}\text{CO}_2\text{H}$ from the KMnO_4 -oxidation products of pure (I), m.p. 168–172°, $[\alpha]_D -92^\circ$. Therefore, the following formula is adopted for (I).



The ready isomerisation of *l*-pimaric acid (II) to (I) and the change in $[\alpha]$ caused thereby, the production of the acid, $\text{C}_{25}\text{H}_{34}\text{O}_8$, from the maleic anhydride adduct (III) of (II), and the absence of $\text{Pr}^{\beta}\text{CO}_2\text{H}$ from the oxidation products of (II) indicate the formulæ shown for (II) and (III). With SeO_2 (I) gives 6-hydroxyabiatic acid, m.p. 153–155° (with loss of H_2O), and +0.5 H_2O , “double” m.p. 120–130° (decomp.) and 150–155° (decomp.), $[\alpha]_D^{25} -125^\circ$ in EtOH (*Me* ester, m.p. 75–77.5°, $[\alpha]_D -96^\circ$ in EtOH), which gives an acidic *Na* salt, $(\text{C}_{20}\text{H}_{30}\text{O}_4)_4 \cdot \text{C}_{20}\text{H}_{29}\text{O}_3\text{Na} \cdot 2\text{H}_2\text{O}$, m.p. 167–170° (decomp.), $[\alpha]_D^{25} -114^\circ$ in EtOH, with H_2 - PtO_2 gives a mixture of (? stereoisomeric) dihydroabiatic acids, m.p. 157° (clears at 165°), and in boiling AcOH readily loses H_2O to give dehydroabiatic acid (IV), m.p. 171–172°, $[\alpha]_D^{25} -61^\circ$ in EtOH, saturated to Br and KMnO_4 , and having an absorption spectrum typical of similar compounds containing an aromatic ring. The *Na* salt of the OH-acid at



175–200° under N_2 loses H_2O and gives the unsaturated anhydrohydroxyabiatic acid (? V), m.p. 167.5–169.5°, $[\alpha]_D^{25} +21^\circ$ in EtOH (*Me* ester, b.p. 174–178°/3 mm.), reduced (H_2 - PtO_2) to a tetrahydroabiatic acid, m.p. 164–164.5°, $[\alpha]_D^{25} +26^\circ$ in EtOH, and giving $\text{Pr}^{\beta}\text{CO}_2\text{H}$ when oxidised. Nitration of (IV) gives the (? 6:8-)(NO_2)₂-derivative, m.p. 178–185° (decomp.), $[\alpha]_D^{25} +49^\circ$ in COMe_2 (*Me* ester, m.p. 189–189.5°, $[\alpha]_D^{25} +53^\circ$ in COMe_2), previously reported as “dinitroabiatic acid” and also obtained from a “pinabiatic acid.” It is now obtained from abiatic acid which has been heated at 260–270°

and in 50–60% yield from α -pyroabiatic acid, m.p. 171–172°, $[\alpha]_D +41^\circ$ in EtOH. It is considered that heating (I) produces a mixture of (IV) and reduced acids by disproportionation and that the α -pyro-acid is really impure (IV), a view supported by its absorption spectrum, which is weaker than, but otherwise identical with, that of (III). M.p. are corr.

R. S. C.

Arylamides of furoylacetic acid.—See B., 1938, 140.

Preparation of furanic ketones containing several ethylenic linkings. N. MAXIM and (MLLE.) M. POPESCU (Bull. Soc. chim., 1938, [v], 5, 49–53).—The marked halochromic effect of the furan nucleus and of ethylenic linkings when associated with CO in aromatic ketones is illustrated as follows (cf. Maxim and Popescu, A., 1935, 626). ϵ -Keto- ϵ -p-tolyl- α -furyl- $\Delta^{\alpha\gamma}$ -pentadiene, m.p. 77°, yellow, from $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ and furalacetaldehyde (I) [from MeCHO and $\text{C}_4\text{H}_3\text{O}\cdot\text{CHO}$ (II)]; ϵ -keto-*o*-phenyl- α -furyl- $\Delta^{\alpha\gamma\theta}$ -nonatetraene, m.p. 103°, orange-yellow, from $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ and ϵ -keto- α -furyl- $\Delta^{\alpha\gamma}$ -hexadiene (III) [from COMe_2 and (I)]; ϵ -keto- α -difuryl- $\Delta^{\alpha\gamma\theta}$ -nonatetraene, m.p. 121°, orange-yellow, from (I) and (III); ϵ -keto- α -furyl- η -dimethylaminophenyl- $\Delta^{\alpha\gamma}$ -heptatriene, m.p. 121°, red prisms, from $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and (III); ϵ -keto- η -piperonyl- α -furyl- $\Delta^{\alpha\gamma}$ -heptatriene, m.p. 119°, orange-yellow, from piperonal and (III); ϵ -keto- η -anisyl- α -furyl- $\Delta^{\alpha\gamma}$ -heptatriene, m.p. 99°, yellow, from $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and (III); ϵ -keto- α -difuryl- $\Delta^{\alpha\gamma\theta}$ -undecapentaene, m.p. 129°, orange-red, from (III) and α -2-furyl- $\Delta^{\alpha\gamma}$ -pentadienal [from (II) and excess of MeCHO]. E. G. B.

Halochromy of furanic and pyrrolic ketones with conjugated double linkings. N. MAXIM and I. COPUZEANU (Bull. Soc. chim., 1938, [v], 5, 57–63).—The colours of various furanic ketones with two double linkings, $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{R}$ (I) when solid and in H_2SO_4 or HCl solution indicate that the nature and position of R have little halochromic effect. Only OMe and CH_2O_2 have much effect, the colour then inclining towards red or violet. Comparison with earlier results (Maxim and Popescu, A., 1935, 626) for furanic ketones with one double linking shows that the second double linking has a marked halochromic effect, the colours changing from yellow to red or violet. Comparison with the colours of various pyrrolic ketones with a single double linking, $\text{C}_4\text{H}_3\text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{R}$ (II), shows that the pyrrole nucleus has hardly any while the furan nucleus has a very marked halochromic effect. OMe and CH_2O_2 have a halochromic effect with (II) similar to that with (I). Absorption spectra of (I) and (II) in CHCl_3 , H_2SO_4 , and HCl show that replacement of CHCl_3 by H_2SO_4 or HCl sometimes causes a shift of the first band >1500 Å., while the no. of bands is increased 2–3 times. With the exception of OMe, CH_2O_2 , and NMe_2 , the nature and position of R have little effect on the no. and position of bands. The ethylenic linking and the furan nucleus cause a marked displacement of bands, whilst the pyrrole nucleus has no effect. If dry HCl is passed through solutions of (I) in C_6H_6 , reddish-violet compounds are formed,

rapidly losing HCl in air. Various theories of halochromy are outlined.

E. G. B.

Pechmann dyes. Supposed isomerism with Kugel dyes. P. CHOVIN (Compt. rend., 1937, 205, 677—680).—The red dye (I) prepared by Bogert and Ritter (A., 1925, i, 255) by a reaction of Kugel's and stated to be isomeric with the red Pechmann dye (II) is shown to be identical with (II). The white dihydrated acid given by alkaline hydrolysis of (I) yields (II) on dehydration. Differences in colour and reflexion of crystals of (I) and (II) are due to conditions of prep. Thus (II) cryst. from Ac_2O gives either (I) or (II) according to the rate of cooling. Similarly (I) prepared by Kugel's method (A., 1898, i, 198) yields either (I) or (II). All preps. of (I) and (II) and their mixtures melt at 317° and their absorption spectra are identical.

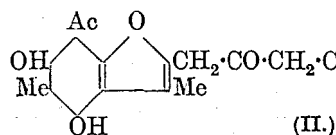
E. G. B.

Anthoxanthins. XVI. Synthesis of herbacetin. L. J. GOLDSWORTHY and R. ROBINSON (J.C.S., 1938, 56—58).—2:4-Dihydroxy- ω :3:6-trimethoxyacetophenone, anisic anhydride, and Na anisate give 7-hydroxy-3:5:8:4'-tetramethoxyflavone, m.p. $269\text{--}270^\circ$, demethylated to 3:5:7:8:4'-pentahydroxyflavone, m.p. $278\text{--}280^\circ$, identical with herbacetin. The $(\text{OH})_5$ -compound yields a $(\text{OAc})_5$ -compound, m.p. $189\text{--}191^\circ$, and a $(\text{OMe})_5$ -compound, m.p. $156\text{--}158^\circ$.

F. R. S.

Lichen substances. LXXXVII. Usnic acid.

IV. Y. ASAHINA, M. YANAGITA, and S. MAYEDA [with, in part, S. KAWAMURA] (Ber., 1937, 70, [B], 2462—2469; cf. A., 1936, 1262; Curd and Robertson A., 1937, II, 347).—Usnic acid (I) with abs. EtOH

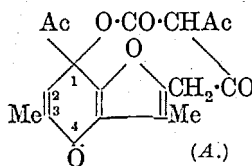


(II.)

at 150° gives Et acetylusnetate (II), m.p. 150° [monosemicarbazone, m.p. 196° (decomp.)], which is

probably (II) since it is hydrolysed by alkali partly to usnetic acid, $\text{C}_{14}\text{H}_{14}\text{O}_6$, m.p. 202° (decomp.) (Et ester, m.p. 147°), and partly to CO_2 and acetylusnetol [deacetyldecarbousnic acid], m.p. $197\text{--}198^\circ$. Triacetyldecarbousnic acid is optically inactive in CHCl_3 . Usnetic acid, which contains 1 O more in its mol. than does (I), into which it is readily transformed by Zn and AcOH, is transformed by EtOH at $100\text{--}105^\circ$ into Et r-isohydroxyacetusnetate, $\text{C}_{18}\text{H}_{20}\text{O}_8$ (III), m.p. 145° (decomp.), hydrolysed by conc. KOH to r-isohydroxyusnetic acid, m.p. 186° after giving a brown-red distillate at about 175° . (III) is deoxidised by Zn and AcOH to Et acetusetate, m.p. 149° . Similarly, d-usnetic acid, m.p. $143\text{--}144^\circ$ (decomp.) after becoming red at about 135° , $[\alpha]_D^{25} +388.6^\circ$ in CHCl_3 , is converted by EtOH at $100\text{--}105^\circ$ into Et d-isohydroxyacetusnetate, m.p. 124° (decomp.), $[\alpha]_D^{25} +127.4^\circ$ in CHCl_3 . From this it follows that O very probably enters not in the 1:3-diketo-side-chain but in the previously-assumed coumarone nucleus in which an asymmetric C is initially present. To explain the structure of this unknown nucleus it must be recognised that (I) when transformed into decarbousnic acid forms a true phloroglucinol nucleus and loses its optical activity whereas when oxidised by KMnO_4 it adds 1O and the usnetic acid thus formed yields an

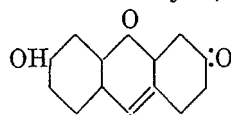
alcoholysis product with asymmetric C. Hence (I) is probably A. On oxidation with KMnO_4 it first adds 2 OH at $\text{C}_{(2)}$ and $\text{C}_{(3)}$ and then loses H_2O with production of usnetic acid (as A, but with OH at 4). During lactone fission migration of the quinol OH is no



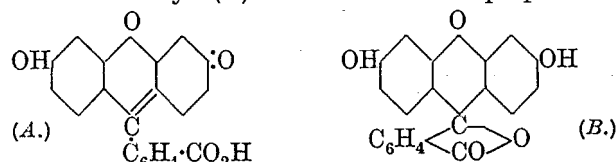
(A.)

longer possible so that the optical activity persists. When reduced it absorbs H at $\text{C}_{(2)}$ and $\text{C}_{(3)}$ and the H_2 -derivative loses H_2O with production of (I). Similarly (III) is hydrogenated in the positions 2 and 3 and the product by loss of H_2O and aromatisation of the quinol nucleus passes into (II). According to the new formulation the Ac groups of Schöpf's diacetylusnetic acid must reside in the furan side-chain and exist partly at any rate in union with C. The feebly acidic properties, positive reaction with FeCl_3 , and the conversion by boiling 60% AcOH into diacetyldecarbousnic acid are in harmony with this view. d-Diacetylusnetic acid is reduced (Pd-C in EtOAc) to d-dihydrodiacetylusnetic acid, m.p. 151° , $[\alpha]_D^{20} +5.52^\circ$ in CHCl_3 , hydrolysed by conc. H_2SO_4 at room temp. to l-dihydrousnetic acid, m.p. 150° , $[\alpha]_D^{20} -83.84^\circ$ in CHCl_3 . Similarly, l-diacetylusnetic acid is reduced to l-dihydrodiacetylusnetic acid, m.p. 151° , $[\alpha]_D^{20} -5.38^\circ$ in CHCl_3 , whence d-dihydrousnetic acid, m.p. $150\text{--}151^\circ$, $[\alpha]_D^{20} +81.73^\circ$ in CHCl_3 . d-Diacetyltetrahydrodeoxyusnetic acid has m.p. 194° , $[\alpha]_D^{20} +27.7^\circ$ in CHCl_3 . H. W.

Structure and absorption of coloured substances. Isomeric forms of fluorescein. P. RAMART-LUCAS (Compt. rend., 1937, 205, 1409—1411).—Measurements of the absorption spectra of fluorescein (I) and its Me_2 ether (II) and of resorcinolbenzein (III) show that (I) can yield an equilibrium mixture of the coloured, fluorescent quinonoid form (A) and the colourless, non-fluorescent, lactoid variety (B). The relative proportions



(A.)



(B.)

of the two forms vary with the nature of the solvent. In EtOH the mol. proportion of (A) : (B) = 1 : 140. In Et_2O (B) is present almost exclusively. Since the quinonoid Et esters of (I) and (III) have bands superposable on those of free (I) the ionoid structure of Wizinger cannot readily be maintained. In alkaline solution (I), its quinonoid ester, and (III) have nearly the same spectra and hence the same p-quinonoid structure; the presence of CO_2H does not considerably modify the absorption of the two former substances. In MeOH-HCl , (I) and (II) afford hydrochlorides of closely similar spectra, and they therefore have the same structure. This cannot be lactoid since they have visible colour and the lactoid di-ether cannot assume the p-quinonoid form. It is probable that they should be assigned the o-quinonoid formula with oxonium O, as generally used for the hydrochloride of (I).

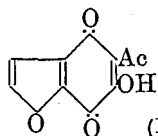
H. W.

Dioxan and its derivatives. VI. Action of di- and tri-chloro- and di- and tri-methyl deriv-

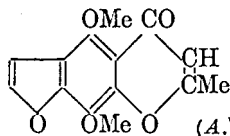
atives of ethyl alcohol on 2:3-dichloro-1:4-dioxan. J. BÖESEKEN, F. TELLEGEN, and M. PLUSJÉ (Rec. trav. chim., 1938, 57, 73—78).—2:3-Dichloro-1:4-dioxan (I) with $\text{CCl}_3\cdot\text{CH}_2\cdot\text{OH}$ in C_6H_6 yields 3-chloro- (II), b.p. 160—190°/20 mm., m.p. 77—78°, converted by boiling EtOH into 3-ethoxy-, b.p. 88—95°/20 mm., and by $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{OH}$ in C_6H_6 into 3- β -chloroethoxy-2- $\beta\beta$ -trichloroethoxy-1:4-dioxan, b.p. 180—183°. With $\text{CHCl}_3\cdot\text{CH}_2\cdot\text{OH}$ and $\text{CH}_3\text{Bu}^\gamma\text{OH}$ (II) does not react. With Pr^βOH , (II) yields 2- $\beta\beta$ -trichloroethoxy-3-isopropoxy-, b.p. 155—165°, and (I) gives 2:3-diisopropoxy-1:4-dioxan, b.p. 123—129°.

E. I.

Natural chromones. I. Constitution of kellen (from *Ammi visnaga*). E. SPÄTH and W. GRUBER (Ber., 1938, 71, [B], 106—113; cf. A., 1931, 73).—Kellen (I), m.p. 154—155° (vac.), is $\text{C}_{14}\text{H}_{12}\text{O}_5$. It is smoothly converted by 1% aq. KOH into AcOH and kellinone [5-hydroxy-3:6-dimethoxy-4-acetylbenzofuran] (II), m.p. 99—101° [acetate, m.p. 73·5—74°; *Et ether* (III), b.p. 120—130° (bath)/1 mm., and its semicarbazone, m.p. 166—167° (vac.; slight decomp.)], which gives a green colour with FeCl_3 . Oxidation of (II) in abs. EtOH with fuming HNO_3 gives the ketone (IV), m.p. 170—172° (vac.; decomp.),



(IV.)



(A.)

thus establishing the position of the OMe in (I) and (II). Oxidation of (I) with alkaline H_2O_2 gives furan-2:3-dicarboxylic acid. Ozonisation of (III) leads to 2-hydroxy-3:6-dimethoxy-4-ethoxy-5-acetylbenzaldehyde; this is completely ethylated with KOH and Et_2SO_4 and then oxidised by KMnO_4 in aq. COMe_2 to 3:6-dimethoxy-2:4-diethoxyacetophenone-5-carboxylic acid (V), the *Me* ester of which affords a semicarbazone, m.p. 202—204° (vac.; decomp.). Decarboxylation of (V) by Cu powder in boiling quinoline leads to 3:6-dimethoxy-2:4-diethoxyacetophenone, b.p. 120—130° (bath)/0·05 mm., characterised as the semicarbazone, m.p. 184—187° (vac.; decomp.). This is obtained synthetically from 2:4-dihydroxy-3:6-dimethoxyacetophenone. Therefore (I) is A. Ac_2O and NaOAc at 160° convert (II) into 3-acetylkellen, m.p. 195—196°, which with aq. Na_2CO_3 gives AcOH and (I).

H. W.

Pyrrole-2-carboxylic acid and amides derived therefrom. N. MAXIM, I. ZUGRAVESCU, and I. FULGA (Bull. Soc. chim., 1938, [v], 5, 44—48).—An improved prep. of pyrrole-2-carboxylic acid is from its *Et* ester, prepared from Mg pyrrol bromide and ClCO_2Et (cf. Oddo, A., 1909, i, 672). With PCl_5 it gives the chloride, from which are obtained the diethylamide, m.p. 99·5°, methyl-, m.p. 147°, and ethyl-, m.p. 123°, -anilides, and diphenylamide, m.p. 173°.

E. G. B.

Dimethyloxindoles. A. WAHL and V. LIVOV-SCHÜ (Compt. rend., 1937, 205, 738—740).—Cyclisation of 2:4-dimethylchloroacetanilide with AlCl_3 affords a compound, $\text{C}_{10}\text{H}_{11}\text{ON}$, m.p. 153°, different from 5:7-dimethyloxindole (carbomesyl) prepared by Wispek

(A., 1883, 1095) as it does not react with aldehydes and is probably a methyldihydrocarbostyryl. 2:6-Dimethylchloroacetanilide similarly affords a dimethyloxindole, m.p. 170° (benzylidene derivative, m.p. 212°), so that the structures of 4:7- and 5:7-dimethyloxindole (cf. A., 1937, II, 115) remain in doubt.

J. L. D.

Isatin derivatives and indigoid vat dyes.—See B., 1938, 143.

Complex salts of amino-acids and peptides.—See A., I, 155.

Preparation of 8-nitro-6-methoxyquinoline. I. P. STRUKOV (Prom. Org. Chim., 1937, 4, 523—524).—Glycerol 350, 85% H_3AsO_4 160, *m*-nitro-*p*-anisidine 160, and H_2SO_4 160 g. are heated under reduced pressure at 100—110° until distillation of H_2O ceases; heating is then continued under reflux at 115—120°, with gradual addition of 120 g. of H_2SO_4 during 2·5 hr. The product is poured into ice- H_2O after 7 hr., and the ppt. of 8-nitro-6-methoxyquinoline (78% yield) is dried at 50°.

R. T.

Condensation of acetylene with aromatic amines in presence of Cu_2Br_2 . XV. N. KOZLOV and L. OLIFSON (J. Gen. Chem. Russ., 1937, 7, 2301—2305).— NH_2Ph or *o*-, *m*-, or *p*-toluidine, COMe_2 , and C_2H_2 in presence of CuBr yield respectively 2:4-dimethyl- or 2:4:8-, 2:4:7-, or 2:4:6-trimethyl-quinoline.

R. T.

Modifications of cobalt quinaldinate. N. K. DUTT (J. Indian Chem. Soc., 1937, 14, 572—573).—By mixing cold neutral solutions of a *Co* salt with *Na* quinaldinate a cream-coloured *Co* quinaldinate-2-carboxylate, $+2\text{H}_2\text{O}$, is formed. Hot and slightly acid solutions give a red variety (anhyd.), obtainable from the first by heating above 160°.

F. L. U.

Synthesis of isoquinoline derivatives. II. W. KRABBE, H. H. BÖHLK, and K. H. SCHMIDT (Ber., 1938, 71, [B], 64—76; cf. A., 1936, 1124).—Substituted vinylamines are formed frequently if not invariably as intermediate products of the conversion of acylamidocarbinols into isoquinoline derivatives according to Pictet and Gams. $\text{NH}_2\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$ (I) is transformed by cold Ac_2O into diphenylacetamidomethylcarbinol, m.p. 141°, which is converted by P_2O_5 in boiling C_6H_6 into acet- $\beta\beta$ -diphenylvinylamide, m.p. 166°, or under more drastic conditions into 4-phenyl-1-methylisoquinoline, m.p. 80° (hydrochloride; picrate, m.p. 206°). This has the same action as papaverine on the smooth muscle but is badly resorbed when administered parenterally. $\text{NH}_2\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{OH}$ is converted by short treatment with boiling Ac_2O into its *N*-*Ac* derivative, m.p. 260°, transformed by P_2O_5 in boiling PhMe into acet- $\alpha\beta$ -triphenylvinylamide, m.p. 90°, and 3:4-diphenyl-1-methylisoquinoline, m.p. 156° [hydrochloride; picrate, m.p. 196° (decomp.)]. β -Benzamido- $\alpha\alpha\beta$ -triphenylethyl alcohol, m.p. 273°, passes under somewhat drastic conditions into 1:3:4-triphenylisoquinoline, m.p. 191° (hydrochloride; picrate, m.p. 156°). Gradual addition of anhyd. HCO_2H to (I) in PhMe affords the corresponding formate, m.p. 153—157° (slight decomp.), which passes at 160° into diphenylformamidomethylcarbinol, m.p. 167° after softening at 140°; this when rapidly distilled under

atm. pressure gives *form*- $\beta\beta$ -diphenylvinylamide, m.p. 174°, or when treated with P_2O_5 in boiling xylene 4-phenylisoquinoline, m.p. 82° (*hydrochloride*, m.p. 185—195° after softening; *picrate*, m.p. 209—210°), also obtained similarly from the amide. It is oxidised by $KMnO_4$ to *o*- $C_6H_4Bz\cdot CO_2H$ and 3-phenylpyridine-4 : 5-dicarboxylic acid, m.p. 225—230°, decarboxylated by distillation with CaO to 3-phenylpyridine. Ozonisation of benz- $\beta\beta$ -diphenylvinylamide in $CHCl_3$ gives a solid ozonide (converted by boiling H_2O into $COPh_2$ and NH_2Bz) or in HCO_2H gives $COPh_2$ and formylbenzamide, m.p. 112°. The amide with boiling $KOH\text{--}EtOH\text{--}H_2O$ gives only a pale, resinous product from which an individual could not be isolated; with $HCl\text{--}EtOH\text{--}H_2O$ the main products are $CHPh_2\cdot CHO$ and $BzOH$ or $EtOBz$. Restricted treatment of (I) with P_2O_5 in boiling C_6H_6 gives *di-aa*-diphenylvinylamine, m.p. 144—146°. 1 : 4-Diphenylisoquinoline (*hydrochloride*) has m.p. 131°. H. W.

Complexes of polynitro-compounds. II. Compounds of polynitro-substances with derivatives of 1-keto-1 : 2 : 3 : 4-tetrahydrocarbazole. A. KENT and D. McNEIL (J.C.S., 1938, 8—11).—The following have been prepared: cyclohexane-1 : 2-dione-1-m-tolylhydrazone, m.p. 156—158°, -1-(6'-cyano-m-tolylhydrazone), m.p. 123°, -2-(4'-nitrophenylhydrazone)-1-(6'-cyano-m-tolylhydrazone), m.p. 214—215°, and -1-*o*-carboxyphenylhydrazone, m.p. 185—186°; 4-methylcyclohexane-1 : 2-dione-2-phenylhydrazone, m.p. 139—141°; 1-keto-2-methyltetrahydrocarbazole-p-nitrophenylhydrazone, m.p. 226—228°; 1-keto-3-, m.p. 194—195° (p-nitrophenylhydrazone, m.p. 265—267°), and 1-keto-4-methyltetrahydrocarbazole, m.p. 131° (p-nitrophenylhydrazone, m.p. 227—229°); 1-keto-tetrahydrocarbazole-8-carboxylic acid, m.p. 279—281° (p-nitrobenzyl ester, m.p. 189°); 1-keto-6-methyltetrahydrocarbazole-p-nitrophenylhydrazone, m.p. 260° (decomp.); and 1-keto-5(or 7)-, m.p. 160—161°, and -7(or 5)-methyltetrahydrocarbazole, m.p. 196°. These substances yield the following mol. compounds, where X is *s*- $C_6H_3(NO_2)_3$, Y is picric acid, Z is *m*- $C_6H_4(NO_2)_2$, and K is 1-ketotetrahydrocarbazole: XA , m.p. 180°, XA_2 , m.p. 186—187°, and YA , m.p. 154—155° ($A = 2$ -methyl-K); XB_2 , m.p. 187—188°, and YB_2 , m.p. 169° ($B = 3$ -methyl-K); XC_2 , m.p. 177°, and YC_2 , m.p. 157—159° ($C = 4$ -methyl-K); XD_2 , m.p. 190—192°, and YD_2 , m.p. 158—159° [$D = 5$ (or 7)-methyl-K]; XE , m.p. 174—176°, YE , m.p. 156—158°, and ZE ($E = 6$ -methyl-K); XF_2 , m.p. 201—203°, and YF_2 , m.p. 183° [$F = 7$ (or 5)-methyl-K]; XG , m.p. 179—180°, YG , m.p. 161—162°, and ZG_2 , ($G = 8$ -methyl-K); XP , m.p. 229—231°, and YP , m.p. 212—214° (decomp.) ($P = 5 : 6$ -benzo-K); and XQ , m.p. 240—241°, and YQ , m.p. 220—222° (decomp.) ($Q = 7 : 8$ -benzo-K). The properties of the compounds are discussed. F. R. S.

meso-Derivatives of acridine. VIII. New method of preparation of N-alkylacridones. N. S. DROZDOV (J. Gen. Chem. Russ., 1937, 7, 2292—2297).—5-Phenoxyacridine derivatives react with *p*- $C_6H_4Me\cdot SO_3H$ esters to yield 10-alkylacridones, of which the following appear to be new: 3 : 10-di-methylacridone, m.p. 150—151°, 3-methoxy-, m.p. 147—148°, 2-chloro-7-methoxy-10-methyl-, m.p. 245—246°, and -10-ethylacridone, m.p. 223—225°.

2-Chloro-5-phenoxy-7-methoxyacridine when heated in acid solution yields 2-chloro-7-methoxyacridone, m.p. >300°, from which 2-chloro-7-methoxy-5-*p*-dimethylamino-phenylacridine, m.p. 197.5—198°, is obtained by heating at 100° with $NPhMe_2$ and $POCl_3$. R. T.

Chemotherapeutic studies in the acridine series. III. 4-Amino-, 1 : 3-, 1 : 7-, and 3 : 6-diamino-acridines. A. ALBERT and W. H. LINNELL (J.C.S., 1938, 22—26).—*o*- $C_6H_4Cl\cdot CO_2Na$, 3 : 5-(NO_2) $_2C_6H_3\cdot NH_2$, and Cu give 3' : 5'-dinitrodiphenylamine-2-carboxylic acid (I), m.p. 263°; the 4 : 3'-acid, m.p. 229°, is similarly obtained. Reduction of the (NO_2) $_2$ -acid with $SnCl_2\text{--}AcOH$ yields 2' : 4'-diaminodiphenylamine-2-carboxylic acid hydrochloride, m.p. 252°, the stannichloride of which with $Sn\text{--}HCl$ affords a compound, described as 1 : 3-diaminoacridone (Jourdan, A., 1885, ii, 987), and apparently a lactam, which is acetylated to 2' : 4'-bisacetamidodiphenylamine-2-carboxylic acid 1 : 2-lactam, m.p. 307°. $POCl_3$ and (I) give 2 : 4-dinitroacridone, and 5 : 4'-dinitrodiphenylamine-2-carboxylic acid with $POCl_3$ yields 5-chloro-2 : 7-dinitroacridine, m.p. 233°. 1 : 3-Dinitroacridine is reduced ($SnCl_2\text{--}AcOH$) to 1 : 3-diaminoacridine, m.p. 225° (decomp.), and 1 : 7-dinitroacridone is similarly reduced to 1 : 7-diaminoacridone, chars at 330°. 4-Aminoacridone hydrochloride is reduced with $Na\text{--}Hg$ to 4-aminoacridine (+2 H_2O), m.p. 181°, and 1 : 7-diaminoacridone is converted similarly into 1 : 7-diaminoacridine, m.p. 126°. 3 : 6-Diaminoacridine, m.p. 322°, may be similarly obtained. The presence of 1- and 4- NH_2 substituents leads always to compounds which are non-fluorescent in alcoholic solution, even when the corresponding substances without these groups fluoresce actively. The preliminary bacteriological tests indicate that all the compounds containing a 1- NH_2 are without antiseptic effect, whereas the 4- (as well as the 5-, 3-, and 2-) NH_2 greatly increases the antiseptic activity. F. R. S.

5-isoButyl- and -propyl-5-crotylbarbituric acid.—See B., 1938, 226.

Glyoxalines. II. R. WEIDENHAGEN and H. WEGNER (Z. Wirts. Zuckerind., 1937, 87, 755—777; cf. A., 1935, 1380, 1507).—*p*-Toluoylecarbonyl acetate, $Cu(OAc)_2$, CH_2O , and NH_3 in $MeOH$ at 100° afford 4(5)-*p*-tolylglyoxaline, m.p. 116—117° (*Cu* derivative; *picrate*, m.p. 210°). 4(5)-*p*-Ethylphenyl-, m.p. 127—128° (*Cu* derivative; *picrate*, m.p. 197°), and 4(5)-*p*-isopropylphenyl-, m.p. 114—115° (*Cu* derivative; *picrate*, m.p. 186—187°), -glyoxaline are obtained similarly. These compounds generally depress the blood pressure but have little action on the uterus. The halogen in 4(5)-*p*-chlorophenyl-, m.p. 147° (*Cu* compound; *picrate*, m.p. 219—220°), and 4(5)-*p*-bromophenyl-, m.p. 142° (*Cu* salt; *picrate*, m.p. 142°), -glyoxaline is so firmly combined that it cannot be replaced by other substituents. 2'-Furyl-4(5)-phenylglyoxaline, m.p. 180° (decomp.) [*Cu* compound; *hydrochloride*, m.p. 275—276°; *picrate*, m.p. 204° (decomp.)], is obtained from benzoylcarbinol, $Cu(OAc)_2$, and furfuraldehyde. 4(5)- β -Naphthylglyoxaline (I), m.p. 170—171° [*Cu* derivative; *picrate*, m.p. 215°; *hydrochloride*, m.p. 219—220° after slight softening;

nitrate, m.p. 185° (decomp.)], is described. Addition of the requisite amounts of I to an alkaline solution of (4)5-*p*-carboxyphenylglyoxaline gives *monoiodo*-, m.p. 240° (decomp.), or *di-iodo*-, m.p. 234—235° (decomp.), -*p*-carboxyphenylglyoxaline. 2:5-Di-iodo-4(5)-*p*-sulphophenylglyoxaline dihydrate is obtained similarly. These compounds are highly toxic. Attempted iodination of glyoxaline-4(5)-carboxylic acid causes decarboxylation with production of 2:4:5-tri-iodoglyoxaline. 4(5)-Phenylglyoxaline with anhyd. K_2CO_3 and pyridinium-1-sulphonic acid at 10—15° gives 4(5)-phenylglyoxaline-1-sulphonic acid, which becomes translucent at 210° (*K* salt). 4(5)- β -Naphthylglyoxaline-1-sulphonic acid, becoming translucent at 200—210°, m.p. indef. (*K* salt), and glyoxaline-1-sulphonic acid, m.p. 221—222° (*K* salt), are obtained similarly. With fuming H_2SO_4 at 100° (I) yields 4(5)-sulpho- β -naphthylglyoxaline, m.p. indef. The prep. of the following -glyoxalines demonstrates the possibility of extension of the synthesis to acyloins: 4:5-dimethyl-, 2:4:5-trimethyl-, 4:5-diphenyl-, m.p. 218° (*picrate*, m.p. 231—232°); 2:4:5-triphenyl-, m.p. 265—266° (*picrate*, m.p. 235°, after slight softening); 4:5-difuryl-, m.p. 162—163° (decomp.) [*Cu* compound; *hydrochloride*, m.p. 196° (decomp.); *picrate*, m.p. 222—223° (decomp.) after darkening]; 2:4:5-trifuryl-, m.p. 202° (decomp.) (*hydrochloride*, m.p. 141°; a *picrate* could not be obtained). Fructose, $Cu(OAc)_2$, CH_2O , and NH_3 in boiling H_2O afford 4(5)-hydroxymethylglyoxaline, apparently with intermediate formation of $CO(CH_2OH)_2$. The following monoalkylamides are obtained by heating the requisite *Me* or *Et* ester and primary amine at about 160°: glyoxaline-4(5)-carb-methylamide, m.p. 145° after slight softening (*picrate*, m.p. 196°); -ethylamide, m.p. 161—162° (*picrate*, m.p. 193—194°); -propylamide, m.p. 121—122° (*picrate*, m.p. 150°); -allylamide, m.p. 130° (*picrate*, m.p. 171—172°). These compounds have only slight toxicity but the pharmacological action is unimportant. The method cannot be applied to the prep. of the dialkylamides. However, the acid is transformed by slightly moist PCl_5 at 110—120° into glyoxaline-4(5)-carboxyl chloride which with an aq. solution of the requisite *sec.* amine gives the following glyoxaline-4(5)-carb-dimethylamide, b.p. 165—170°/0.4 mm., m.p. 90—91° [*oxalate*, m.p. 204° (decomp.); *picrate*, m.p. 200—202°]; -diethylamide, b.p. 168—175°/0.4 mm. [*oxalate*, m.p. 166° (slight decomp.); *picrate* (+ H_2O), m.p. (anhyd.) 158—159°]; -dipropylamide, b.p. 180—190°/0.4—0.5 mm., m.p. 69—70° [*oxalate*, m.p. 160—161°; *picrate* (+ H_2O), m.p. (anhyd.) 147—148°]. *o*-Diamines of the C_6H_6 series react with aldehydes in H_2O or $EtOH$ in presence of $Cu(OAc)_2$ and the benzimidazoles separate as complex *Cu* salts when the mixtures are gently warmed or heated not above 100°. The complexes in hot H_2O or H_2O - $EtOH$ are decomposed by H_2S and the bases usually separate pure and in good yield from the filtrates from the *CuS*, after concn. if necessary. The following -benzimidazoles are thus obtained: 2-methyl-, m.p. 175—176°; 2-ethyl-, m.p. 174—175°; 2-*n*-propyl-, m.p. 157—159°; 2-isopropyl-, m.p. 228°; 2-*n*-butyl-, m.p. 149—151°; 2-isobutyl-, m.p. 186—187°; 2-*n*-amyl-, m.p. 159—161°; 2-*n*-hexyl-,

m.p. 136—138°; 2-dimethylheptadienyl- (probably a mixture of stereoisomerides), m.p. (indef.) 102° after softening; 2-phenyl-, m.p. 290°; 2-*o*-nitrophenyl-, m.p. 190—193° [*hydrochloride*, m.p. 291° (decomp.)]; 2-*m*-nitrophenyl- (+ H_2O), m.p. 204°; 2-*p*-nitrophenyl- [*hydrochloride*, m.p. 310° (decomp.)]; 2-4'-hydroxy-3'-methoxyphenyl-, m.p. 221—222°; 2-*p*-anisyl-, m.p. 228—230°; 2-3':4'-methylenedioxyphenyl-, m.p. 249°; 2-styryl-, m.p. 201—202°; 2-furyl-, m.p. 285—286°. *Et* 2-ethyl-, m.p. 151°, and 2-hexyl-, m.p. 238—240°, -benzimidazole-5-carboxylate are described. 1:2- $C_{10}H_6(NH_2)_2$ and the requisite aldehyde afford 2-isopropyl-, m.p. 239—240° (*Cu* salt), and 2-hexyl-, m.p. 199—202°, -1':2'-naphth-iminazole. H. W.

Action of ammonia on benzil. D. DAVIDSON, M. WEISS, and M. JELLING (*J. Org. Chem.*, 1937, 2, 319—327).—The course of the reaction of NH_3 with benzil (I) and the structures of the products, viz., benzilimide (II), benzilam (III), imabenzil (IV), and lophine (V), are discussed. (II) is shown to be *N*-desylbenzamide (McKenzie and Barrow, *J.C.S.*, 1913, 103, 1331) [*oxime*, m.p. 197—203° (corr.)], synthesised by benzylation of $COPh\cdot CHPh\cdot NH_2$, and not 2-hydroxy-2:4:5-triphenyloxazoline (Japp, *ibid.*, 1886, 49, 473). $PhCHO$, (I), and NH_3 give (V) only and a course for the reaction between (I) and NH_3 is therefore suggested which avoids $PhCHO$ as an intermediate (Japp, *loc. cit.*). With NH_3 (I) gives $COPh\cdot CPh(OH)\cdot NH_2$ (VI), which with (I) gives $COPh\cdot CPh(OH)\cdot N:CPh\cdot COPh$, the labile $:C(Ph)\cdot C(O)\cdot$ linking of which is readily hydrolysed to $COPh\cdot CPh(OH)\cdot N:CHPh$ (VII) and $BzOH$. Cyclo-dehydration of (VII) gives (III) (2:4:5-triphenyloxazoline) by way of (II). This mechanism is analogous to that of the formation of α -acylaminoacids from NH_3 and α -keto-acids. The formation of (V) from NH_3 , $PhCHO$, and (I) in $EtOH$ is explained by formation of $CHPh(NH_2)_2$ and condensation of this with (I) to yield $\begin{matrix} CPh\cdot N \\ CPh\cdot N \end{matrix} > CHPh$, which changes into (V) (2:4:5-triphenylglyoxaline). The mechanism is analogous to the formation reaction of hydrobenzamide. When (I) reacts with NH_3 , (V) is formed from (II) by action of NH_3 , which explains the absence of (II) in the later stages of the reaction, while (III) does not react with NH_3 and is thus among the final products. (IV), which is a primary product but disappears later, is converted by acids into (II), (I), and NH_3 , and is assumed to be formed by condensation of (VI) with (II), i.e., is 5:6-dihydroxy-1-benzoyl-2:3:5:6-tetraphenyl-1:2:5:6-tetrahydro-pyrazine.

Benzil and NH_4OAc in boiling glacial $AcOH$ give (V) (90%) with some (III), owing to the suitability of $AcOH$ as a medium for converting acyldesylamines into glyoxalines by NH_3 . Thus (II) and *N*-desylacetamide (VIII), m.p. 137° (corr.), give respectively (V) and 4:5-diphenyl-2-methylglyoxaline (IX), m.p. 243° (corr.), under these conditions. With NH_2Ph , (II) and (VIII) give respectively tetraphenylglyoxaline, m.p. (new) 221° (corr.), and 1:4:5-triphenyl-2-methylglyoxaline, m.p. 197° (corr.). With fused NH_4OAc or HCO_2NH_4 , (I) gives at high temp. mainly

(III). The prep. of glyoxalines from (I), RCHO , and NH_3 is improved by using AcOH as solvent; RCHO may be replaced by their NH_2 derivatives or reversible polymerides. Thus (I), NH_4OAc , and $(\text{CH}_2)_6\text{N}_4$, paraldehyde, and PhCHO (or hydrobenzamide) in AcOH give nearly quant. yields of 4:5-diphenylglyoxaline, (IX), and (V), respectively.

E. G. B.

Action of ammonia on benzoin. D. DAVIDSON, M. WEISS, and M. JELLING (J. Org. Chem., 1937, 2, 328—334).—Benzoin (I) with NH_3 in AcOH gives mainly amarone (II) (tetraphenylpyrazine; cf. Japp and Wilson, J.C.S., 1886, 49, 825), 4:5-diphenyl-2-methylglyoxaline (III), and some dihydroamarone (IV). The probable course of the reaction is conversion of (I) into $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}\cdot\text{NH}$ (V), tautomerising to $\text{COPh}\cdot\text{CHPh}\cdot\text{NH}_2$ (VI), which condenses either with itself to give (IV), oxidising to (II), or with AcOH to give its Ac derivative, which with NH_3 gives (III). Formation of (IV) is shown by the orange colour of the reacting mixture. Destruction of this by HNO_3 yields a further ppt. of (II). The yield of (II) is a max. in presence of air. The above mechanism is confirmed by replacement of (I) by the hydrochloride of (VI), when the yields of (II) and (III) are not affected. In EtCO_2H instead of AcOH , the Et analogue is formed in place of (III). In anhyd. $\text{AcOH}\cdot\text{HCO}_2\text{H}$, *N*-desylformamide, m.p. 122° , is formed, giving, with NH_3 , 4:5-diphenylglyoxaline. The initial formation of (V) in the reaction in AcOH is confirmed by replacing (I) by its esters, when oxazoles are formed in addition to glyoxalines. Thus esters $\text{COPh}\cdot\text{CHPh}\cdot\text{O}\cdot\text{CO}\cdot\text{R}$ ($\text{R} = \text{Me}$ or Ph) with NH_3 give the corresponding 2-substituted-4:5-diphenyloxazoles (VII). The intermediates $\text{NH}_2\cdot\text{CPh}\cdot\text{CPh}\cdot\text{O}\cdot\text{CO}\cdot\text{R}$ are probably formed, giving either (VII) by cyclodehydration or $\text{OH}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{R}$ and $\text{COPh}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{R}$ by successive acyl migration and tautomerisation. The last two with NH_3 give 2-substituted 4:5-diphenylglyoxalines.

E. G. B.

Heteropolar compounds. IV. New derivatives of 2-thio-4-hydroxy-1:2:3:4-tetrahydroquinazoline. C. V. GHEORGHIU and B. ARVENTI (Bull. Soc. chim., 1938, [v], 5, 38—43; cf. A., 1937, II, 351).—The effect of 4-substitution on the ionic dissociation of 2-thion-4-hydroxy-1:2:3:4-tetrahydroquinazoline has been studied by the prep. of the following derivatives by condensation of $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ with the appropriate thiocarbimide alone or in EtOH : 4-hydroxy-2-thion-3:4-diphenyl-, m.p. 183° , 4-phenyl-3- α -naphthyl-, m.p. $171\text{--}174^\circ$, 4-phenyl-3- β -naphthyl-, m.p. 219° , and 4-phenyl-3-allyl-, m.p. $175\text{--}180^\circ$, -1:2:3:4-tetrahydroquinazolines. The ionic dissociations of these compounds, as shown by the duration of the coloration produced in solutions in inert solvents by heat, are $>$ those of the corresponding 2-thion-4-ethoxy-3-allyl-, -3-phenyl-, and -3- α -tolyl-tetrahydroquinazolines. This is to be expected on the assumption that dissociation occurs by fission of the ring between atoms 3 and 4. Ph and α - and β - C_{10}H_7 in the 3-position have much the same effect on dissociation, while allyl has a much greater effect.

E. G. B.

Action of (A) chloropyridine, (B) 2-chloroquinoline, on anthranilic acid. O. SEIDE and G. V. TSCHELINCEV (J. Gen. Chem. Russ., 1937, 7, 2314—2317, 2318—2323).—(A) The substance " α -quinoquinoline," obtained by Reissert (A., 1895, i, 244) from 2-chloropyridine-5-carboxylic acid and anthranilic acid (I), and by R  th (A., 1931, 852) from 2-chloropyridine and (I), and termed by him "pyracridone," is 2:3-dihydrobenzquinazolinone-4, prepared by Seide (A., 1925, i, 159) from 2-aminoquinoline and $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$. R  th's work is repeated, and his various products are shown to have been wrongly identified. In particular, "2-oxalylaminopyridine-3-carboxylic acid" is shown to be impure 4-hydroxyquinazolinone (II), "2-aminopyridine-3-carboxylic acid hydrochloride" is the hydrochloride of (II), and "2-aminopyridine-3-carboxylic acid" is (II); "pyracridone hydrazone" is the hydrazone of 2-pyridylanthranilic acid.

(B) Bose and Sen's synthesis (A., 1932, 66) of benzquinazolinone (III) [hydrochloride, $+\text{H}_2\text{O}$; picrate, m.p. 203° ; platinichloride, decomp. at 327° ; chromate, decomp. at 170° ; methiodide, m.p. 122° (decomp.)], and its hydrolytic conversion into *N*-2-quinolylanthranilic acid (IV) are confirmed. The Na salt of (IV) and PhI in presence of Cu-bronze (3 hr. at the b.p.) yield *N*-phenyl-*N*-2-quinolylanthranilic acid, m.p. $221\text{--}222^\circ$ (decomp.), which with H_2SO_4 at 100° gives *N*-2-quinolylacridone, m.p. 270° . In aq. KOH (12 hr. at room temp.) (III) and KMnO_4 yield 9:10-diketo-1':2':3:2-(3'-indolenino)-3:4-dihydroquinazolinone and 4-keto-2-2'-carboxyphenyl-3:4-dihydroquinazolinone.

R. T.

New derivatives of pyrimidine. W. HUBER and H. A. H  LSCHER (Ber., 1938, 71, [B], 87—100).—The following compounds have been prepared for comparison with the products of the degradation of vitamin- B_1 . The picrate, m.p. $273\text{--}275^\circ$ (decomp.), and hydrochloride, m.p. 240° (decomp.), of 2:6-diamino-, the picrate, m.p. $>300^\circ$, and hydrochloride, m.p. 284° (decomp.), of 4:6-diamino-5-ethylpyrimidine, and the picrate, m.p. $>300^\circ$, and hydrochloride, m.p. $>300^\circ$, of 2:6-diamino-4:5-dimethylpyrimidine. 4:6-Dihydroxy-2-ethylpyrimidine, m.p. 299° (decomp.) (*Na* and *Cu* salts), is obtained from propionamide hydrochloride, $\text{CH}_3\text{CO}_2\text{Et}$, and NaOEt . 4:6-Dihydroxy-2:5-dimethylpyrimidine is converted by boiling POCl_3 into 4:6-dichloro-2:5-dimethylpyrimidine, m.p. 39° , which with $\text{NH}_3\text{--EtOH}$ at 180° affords 4(6)-chloro-6(4)-amino-2:5-dimethylpyrimidine, m.p. $196\text{--}197^\circ$, whence by $\text{NH}_3\text{--EtOH}$ at 250° 4:6-diamino-2:5-dimethylpyrimidine, m.p. $225\text{--}226^\circ$ [picrate, m.p. 285° (decomp.)]; hydrochloride, m.p. 330° with elimination of HCl . 2-Amino-4:6-dimethylpyrimidine in H_2O at 0° with Br in excess affords an intensely red-brown perbromide, which when treated successively with SO_2 and NH_3 gives 5-bromo-2-amino-4:6-dimethylpyrimidine, m.p. $183\text{--}184^\circ$ (picrate, m.p. $201\text{--}203^\circ$), from which Br is removed by Cu-bronze or CuSO_4 and $\text{NH}_3\text{--EtOH}$ at 240° . Cautious addition of 4:6-dihydroxy-2-methylpyrimidine to HNO_3 (d 1.52) at $>20^\circ$ gives 5-nitro-4:6-dihydroxy-2-methylpyrimidine, decomp. $270\text{--}280^\circ$, which with freshly distilled POCl_3 under

strictly defined conditions affords 4:6-dichloro-5-nitro-2-methylpyrimidine, m.p. 37°, converted by NH_3 -EtOH at 0° into 5-nitro-4:6-diamino-2-methylpyrimidine, m.p. 234–235° (decomp.) [picrate, m.p. 233–235° (decomp.)]; hydrochloride, slow decomp. 200–220° with loss of NH_4Cl . Acetamidine hydrochloride and the Na derivative of urethanoformylacetic ester in H_2O containing a slight excess of NaOH gradually yield 5-urethano-4-hydroxy-2-methylpyrimidine, m.p. 260–261° (decomp.) (picrate, m.p. 180–182°; hydrochloride, m.p. >300°). 5-Urethano-4-hydroxy-2-methylpyrimidine with conc. HCl at 120–130° furnishes 4:5-dihydroxy-2-methylpyrimidine, m.p. 231° (decomp.) (K_2 salt). Et_2 acetosuccinate, ψ -ethylthiocarbamide hydrobromide, and KOH yield *Et* 6-hydroxy-2-ethylthiol-4-methylpyrimidine-5-acetate, m.p. 163°. The following condensations of derivatives of $\text{CH}_2(\text{CN})_2$ with amidines and carbamide derivatives are effected by dissolving equiv. amounts of the reactants in EtOH, the amidine or carbamide component being liberated by the requisite amount of NaOEt. Thus are prepared: 6-amino-2-ethylpyrimidine-5-nitrile, m.p. 198° (picrate, m.p. 198–5°), hydrogenated (Pd-C in AcOH containing HCl at room temp.) to 6-amino-5-amino-methyl-2-ethylpyrimidine, m.p. 229°; 6-amino-2-phenylpyrimidine-5-nitrile, m.p. 226° (decomp.) (picrate, m.p. 196°), whence 6-amino-2-phenyl-5-aminomethylpyrimidine dihydrochloride, m.p. 291–292° (corresponding dipicrate, m.p. 226–227°); 6-amino-2-ethylthiolpyrimidine-5-nitrile, m.p. 141°; 2:6-diaminopyrimidine-5-nitrile, gradual decomp. >300°; ethoxyethylidenemalonodinitrile, m.p. 87°; 6-amino-2:4-dimethylpyrimidine-5-nitrile, m.p. 220–5°; 6-amino-2:4-dimethyl-5-aminomethylpyrimidine, m.p. 192–193° (decomp.). H. W.

Pyrimidine derivatives.—See B., 1908, 140.

Synthesis of α -6-methoxytryptophan and of harmine; action of acetaldehyde on tryptophan. D. G. HARVEY and W. ROBSON (J.C.S., 1938, 97–101).— $\text{Et}_2\text{C}_2\text{O}_4$, KOEt, and *o*-nitro-*p*-tolyl Me ether give the K derivative of Et *o*-nitro-*p*-methoxyphenylpyruvate, which with aq. NH_3 - FeSO_4 yields NH_4 6-methoxyindole-2-carboxylate, decarboxylated to 6-methoxyindole; this with CHCl_3 and KOH affords 6-methoxyindole-3-aldehyde and 3-chloro-7-methoxyquinoline. The aldehyde with hydantoin in $\text{C}_5\text{H}_{11}\text{N}$ gives 5-(6'-methoxyindolal)hydantoin, m.p. 311–315°, which is reduced (H_2S) to 5-(6'-methoxyindolylmethyl)hydantoin, m.p. 220°, converted by aq. NH_3 into 6-methoxytryptophan (I), m.p. 263–268°; this compound could not be demethylated. 1-Tryptophan and MeCHO give 3-methyl-3:4:5:6-tetrahydro-4-carboline-5-carboxylic acid, m.p. 295–299°, oxidised ($\text{K}_2\text{Cr}_2\text{O}_7$) to harman in 75% yield. MeCHO and (I) afford 11-methoxy-3-methyl-3:4:5:6-tetrahydro-4-carboline-5-carboxylic acid (+ H_2O), m.p. 244–246°, oxidised to harmine in 40% yield.

F. R. S.

3-Carbazyl-2-indole. S. M. SCHERLIN and A. J. BERLIN (J. Gen. Chem. Russ., 1937, 7, 2275–2277).—*N*-Acetylcarbazole and $\text{CH}_2\text{Cl}\cdot\text{COCl}$ in CS_2 and AlCl_3 (30 min. at 100°, followed by 2 hr. at room temp.) yield *N*-acetyl-3-chloroacetylcarbazole, m.p.

175–177°, hydrolysed to 3-chloroacetylcarbazole, m.p. 207–209° (decomp.). This when heated at 120–130° for 3 hr. yields 3-carbazyl-2-indole, m.p. >300°.

R. T.

Phenazine. (I.) Action of methyl sulphate on phenazine, 1-methoxyphenazine, and 1-hydroxyphenazine. H. HILLEMANN (Ber., 1938, 71, [B], 34–41).—Treatment of phenazine in PhNO_2 with Me_2SO_4 for 7 min. at 100° gives phenazine methosulphate (I), m.p. 155–157°, whereas more protracted action leads to 2-methylphenazine methosulphate (II), m.p. 185–186° (decomp.), also obtained from (I) and Me_2SO_4 . Still more protracted action affords charred matter and a green powder of variable composition, decomp. >250°. Quant. hydrogenation of the blood-red solution of (I) in EtOH gives a max. green intensity after absorption of 1 H. Complete hydrogenation is achieved by addition of 2 H and the solution then becomes colourless. If to this solution an equiv. amount of (I) is added, dark green crystals of the semiquinonoid compound, m.p. 158°, not identical with (II), are obtained. NH_3 in excess and (I) in MeOH give a blue solution from which CHCl_3 removes a black powder of indefinite m.p. With alkali (I) gives a blue solution from which only phenazine could be isolated, whilst SO_2 transforms (I) into dark green crystals which darken at 200° and have m.p. >360°. Similarly short interaction of 1-methoxyphenazine and Me_2SO_4 at 100° gives 1-methoxyphenazine methosulphate (III), m.p. 171–172°, reduced in EtOH by 1 H to a green and by 2 H to a colourless compound. Addition of an equiv. amount of (III) to this colourless solution followed by picric acid gives the semiquinonoid picrate, m.p. 195–196°. More protracted action causes the introduction of Me into the nucleus with production of 1-methoxy-3:7-dimethylphenazine methosulphate, m.p. 168–170° (decomp.). 1-Hydroxyphenazine and Me_2SO_4 rapidly yield the corresponding methosulphate (IV) whereas more prolonged action leads to 1-hydroxy-3-methylphenazine methosulphate, m.p. 163–165°. After very protracted change an unidentified almost black compound, m.p. >250°, is obtained. Mild hydrolysis of (IV) in MeOH by CH_2N_2 in Et_2O or by H_2O followed by NaOAc affords pyocyanine [aurichloride, m.p. 177° (decomp.)].

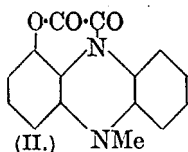
Pyrogallyl carbonate and CH_2N_2 in abs. Et_2O yield the carbonate, m.p. 111–113°, of the 1-Me ether, hydrolysed by boiling H_2O to pyrogallol 1-Me ether, b.p. 148–149°/24 mm. Condensation of the corresponding *o*-quinone with *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ is accompanied by oxidation leading to the production of 2:3-diamino- and 3-amino-2-hydroxy-phenazine; addition of H_3BO_3 brings no improvement. Replacement of PbO_2 by $\text{Pb}(\text{OAc})_4$, CrO_3 , *o*-benzoquinone, tetrabromo-*o*-benzoquinone, or Bz_2O_2 was a failure or gave no advantage. Condensation of PhNO_2 with *o*-anisidine and KOH at 140° to 160° gives small amounts of 2-methoxyazobenzene, m.p. 40–41°, but not 1-methoxyphenazine. H. W.

Phenazine. II. 5:10-Dimethyldihydrophenazine. H. HILLEMANN (Ber., 1938, 71, [B], 42–46).—Gradual addition of phenazine methiodide or methochloride (obtained by treating phenazine

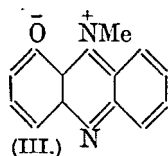
methosulphate successively with picric acid and HCl in MeOH) to MgMeI in Et₂O gives 5:10-dimethyldihydrophenazine (I), m.p. 151—152°, and phenazine (II) derived from initial material which has not entered into the reaction. The constitution of (I) follows from its formation by the successive action of LiEt and MeI on 5-methyldihydrophenazine. The latter substance is readily autoxidised and passage of air through its solution in C₆H₆ causes rapid development of a bluish-red colour; in one instance it was possible to isolate from such a solution almost black, very unstable crystals, m.p. 116—118° after softening at 100°, which are more conveniently prepared from I and Li 5-methyldihydrophenazine. Addition of picric acid to a solution of equal parts of (I) and (II) in EtOH leads to a *picrate*, decomp. 190°, of undecided structure. Attempts to prepare (I) from *o*-C₆H₄(NHMe)₂ and *o*-C₆H₄(NH₂)₂·2HCl in a sealed tube at 220° and from *o*-C₆H₄(NHMe)₂ and *o*-C₆H₄(OH)₂ at 200—210° were not successful. *o*-C₆H₄I₂, *o*-C₆H₄(NHMe)₂, K₂CO₃, and Cu powder in boiling amyl alcohol give a substance, C₁₁H₁₀N or C₂₂H₂₀N₂, m.p. 191°, which has not been identified. *o*-C₆H₄Br·NH₂, PhNO₂, K₂CO₃, and Cu powder afford essentially (II).

H. W.

Phenazine. III. Position of the methyl group in pyocyanine and attempted synthesis of isopyocyanine. H. HILLEMANN (Ber., 1938, 71, [B], 46—52).—1-Hydroxyphenazine methosulphate is reduced by Zn dust and dil. HCl to leucopyocyanine (I); this with (COCl)₂ in CHCl₃—C₂H₅N yields the *oxalyl* compound (II), m.p. 218—222° (decomp.) after softening at 209° in a sealed capillary. Since this compound is hydrolysed by prolonged shaking with H₂O the ·CO·CO· group must be



attached to N and O; this is possible only if in (I) Me is attached to N remote from O. The analogous compound formed from COCl₂ has m.p. 221—222° (decomp.), and is too unstable to recrystallise. In unsuccessful attempts



to synthesise isopyocyanine (III) the following experiments have been performed. 1:2:6-C₆H₃Cl(NO₂)₂ and *o*-NO₂·C₆H₄·NHMe are converted by K₂CO₃ and CuI in boiling amyl alcohol into 2:2':6-trinitrodiphenylmethylamine, m.p. 221—223°. *o*-NH₂·C₆H₄·NHMe and 2:6-dinitrophenyl *p*-toluenesulphonate in boiling C₆H₆ yield 2:6-dinitro-2'-aminodiphenylmethylamine or 2:6-dinitro-2'-methylaminodiphenylamine, m.p. 177°. Ring-closure to the phenazonium system could not be achieved. 3-Nitro-2-aminophenol (IV) is reduced by Na₂S₂O₄ to 2:3-diaminophenol, m.p. 166°. CH₂N₂ and (IV) give only small amounts of 3-nitro-2-aminoanisole, the bulk of the CH₂N₂ appearing to be decomposed catalytically. 3-Nitro-2-aminophenetole, *o*-C₆H₄I·NO₂, K₂CO₃, and Cu powder yield 2:2'-dinitro-6-ethoxydiphenylmethylamine, m.p. 123—125°, converted by KOH and Me₂SO₄ in boiling COMe₂ into 2:2'-dinitro-6-ethoxydiphenylmethylamine, m.p. 125—127°, which could not be hydrolysed satisfactorily. It is reduced by SnCl₂ in AcOH to the compound, C₁₅H₁₉ON₃, m.p. 103—105°.

H. W.

Alloxazine; isoalloxazine (flavin), and lumazine groups. I. Synthesis of 6- or 7-phenyl- and 6:7-diphenyl-lumazines. K. GANAPATI (J. Indian Chem. Soc., 1937, 14, 627—632).—Phenylglyoxal hydrate with 4:5-diaminouracil sulphate (I) gives 6- or 7-phenyl-lumazine, m.p. >330° (Me₂ derivative, m.p. 278°). Benzil and (I) afford 6:7-diphenyl-lumazine, m.p. 310—315°. Piperil (improved prep.) with (I) yields 6:7-di-(3:4-methylenedioxyphenyl)lumazine, m.p. >330°, in small amount, whilst with camphorquinone and (I), 2':3'-camphorolumazine, m.p. >320°, is obtained. F. R. S.

Phthalocyanine-like pigments related to the porphyrins. C. E. DENT (J.C.S., 1938, 1—6).—Phthalimidenecetic acid dihydrate (I) in H₂O at 80° gives methylenephthalimidine (II), m.p. 120—125°, which polymerises on heating. Phthalonitrile, (II), and CuCl₂ yield *Cu* tetrabenzotriazaporphin. 4-Chlorophthalonitrile, (I), and CuCl afford *Cu* trichlorotetrabenzotriazaporphin. *Cu* and *Me* phthalimidenecetates, m.p. 125—127°, do not give pigments in appreciable yield. The new pigments are green to blue and resemble in properties the phthalocyanines. Benzylidene- and ethylidene-phthalimidine have been prepared by new and improved methods. F. R. S.

Light absorption and constitution of some chlorophyll derivatives.—See A., I, 10.

Light absorption of porphyrin dyes; relation to structure.—See A., I, 59.

Action of light on porphyrins. I. Conversion of aetioporphyrin-I into bilirubinoid dyes. H. FISCHER and K. HERRLE (Z. physiol. Chem., 1938, 251, 85—96).—Aetioporphyrin-I in C₅H₅N and in presence of O₂ and NaOEt undergoes photochemical decomp. into a mixture which is separated by treatment with HCl and chromatographic adsorption on Al₂O₃ into a porphyrin, C₃₂H₃₈O₅ or C₃₂H₃₈N₄, decomp. 320°, aetioglucobilin, C₃₁H₃₈O₂N₄, m.p. 238°, a red ketone, C₃₁H₃₆O₃N₄, m.p. 244° (*Cu* salt), reduced by Na—Hg to (?) aetiomesobilirubinogen and by Na₂S₂O₄, and two isomeric dicyclic aldehydes, C₁₆H₂₀O₂N₂. The mechanism of the production of these compounds is discussed. W. McC.

Reaction of salts or esters and anhydrides of monobasic acids with some cyclic ammonium salts containing reactive methyl groups. T. OGATA (Proc. Imp. Acad. Tokyo, 1937, 13, 360—363).—A summary of published work (A., 1934, 422; 1936, 869). The product of interaction of 2-methylbenzthiazole ethiodide and A'O—MOA (A = acyl; M = metal or alkyl) depends on the relative strengths of AOH and A'OH, the radical from the stronger acid forming the 8-substituent of the resulting trimethinethiocyanine. F. R. G.

Aneurin. IX. New synthesis of thiochrome. Synthesis of aneurin. F. BERGEL and A. R. TODD (J.C.S., 1938, 26—28).—2-Thio-7-methyl-1:2:3:4-tetrahydro-1:3:6:8-benzotetrazine, m.p. 275—277° (decomp.), obtained from 4-amino-2-methyl-5-amino-methylpyrimidine hydrochloride and CS(NH₂)₂ or KCNS, with Me α-chloro-γ-acetoxypyrrol ketone (I) gives thiochrome. 4-Amino-2-methyl-5-thioformamidomethylpyrimidine, (I), and AcOH afford O-

acetylneurin chloride hydrochloride, m.p. 205—207°, which is an intermediate product, not hitherto isolated, in the synthesis of aneurin (cf. A., 1937, II, 216). The existence of a low-melting modification of aneurin chloride hydrochloride is confirmed. F. R. S.

N-Methylmyosmine. E. SPÄTH, J. P. WIBAUT, and F. KESZTLER (Ber., 1938, 71, [B], 100—106).—Attempts to resolve an old specimen of dihydronicotyrine (I) into its optical antipodes (cf. Oosterhuis and Wibaut, A., 1936, 1276) by 4:6:4':6'-tetranitro-2:2'-diphenic acid give a product with small $[\alpha]_D$ but the experiments are devoid of constitutional significance since specimens of (I), when preserved, pass into a mixture of nicotine and nicotyrine. Oxidation of (I) by KMnO_4 in dil. H_2SO_4

gives $\text{NHMe} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$, identified as β -p-toluenemethylsulphonamido-propionic acid, m.p. 110—111° (prep. from $\text{CH}_2\text{I} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ described). Therefore (I) is A and may also be regarded as N-methylmyosmine.

The nicotine synthesis of Späth and Bretschneider can therefore be simplified since 3-pyridyl 3'-1'-methyl-2'-pyrrolidonyl ketone is converted by 12N-HCl at 130° into (I), catalytically reduced (Pd-sponge in AcOH) to *dl*-nicotine. The structure A has been assigned by Noga (A., 1915, i, 711) to *isonicotine*; this is not identical with (I) but may possibly be 2:3'-dipyridyl or nicotyrine. The nicotine of Pictet and Rotschy does not appear to be homogeneous. The dihydronicotyrine obtained from idonicotyrine by Pictet and Crépeux is identical with (I).

H. W.

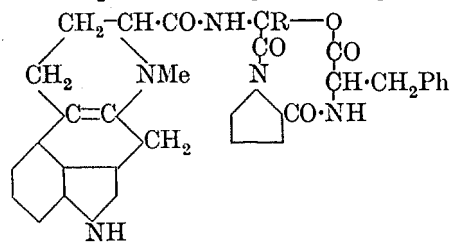
Alkaloids of *Ammodendron Conollyi*. Constitution of ammodendrine. A. ORÉKHOV and N. PROSKURNINA (Bull. Soc. chim., 1938, [v], 5, 29—38).—The *sec.*-base ammodendrine (I), $\text{C}_{12}\text{H}_{20}\text{ON}_2$, $[\alpha]_D^0$, probably contains $\text{N} \cdot \text{CO}$. With alkalis it gives a base, $\text{C}_{10}\text{H}_{18}\text{N}_2$, and AcOH, and so is $\text{C}_{10}\text{H}_{18}(\text{NH})(\text{NAC})$. Hydrogenation (Pt-H_2) of (I) gives *dihydroammodendrine* (II) [*N-Me* derivative (*methiodide*, m.p. 177—180°)], which with alkalis gives AcOH and 2:3'-dipiperidyl. Methylation of (I) followed by hydrogenation and hydrolysis gives *N*-methyl-2:3'-dipiperidyl, identical with that obtained by methylation and hydrogenation of *r*-anabasine. Therefore (II) is 1-acetyl-3- α -piperidylpiperidine. The position of the double linking in (I) is uncertain. It is the only base of this type known in the Leguminosae and occurs in *A. Conollyi* with *d*-sparteine (III), the ratio of (I) to (III) varying with age, indicating possible interconversion. This hypothesis is supported by the simultaneous presence of sparteine alkaloids and anabasine in *Anabasis aphylla*.

E. G. B.

Synthesis of salsolidine. E. SPÄTH and F. DENGEL (Ber., 1938, 71, [B], 113—119; cf. A., 1933, 907).—6:7-Dimethoxy-1-methyl-3:4-dihydroisoquinoline, obtained by the action of P_2O_5 on *N*-acetylhomoveratrylamine, is reduced by Zn and 2N-HCl or catalytically (Pd-sponge in MeOH containing AcOH at 40—45°) to *dl*-6:7-dimethoxy-1-methyl-1:2:3:4-tetrahydroisoquinoline (= *dl*-salsolidine) (I), b.p. 180° (bath)/1 mm., m.p. 53—53.5° [hydrochloride, m.p. 196—197°; picrate, m.p. 201—

201.5° (decomp.); picrolonate, m.p. 241° (decomp.); *Bz* derivative, m.p. 127—128° (vac.); the consts. differ considerably from those recorded by Proskurnina and Orékhov, A., 1937, II, 394]. Pd-sponge dehydrogenates (I) at 180° to 6:7-dimethoxy-1-methylisoquinoline, m.p. 107—108°. Successive treatments of (I) with *d*- and *l*-tartaric acid in H_2O give *l*-salsolidine (II), m.p. 47.5—48.5°, $[\alpha]_D^{25} -59.7^\circ$ in abs. EtOH, and *d*-salsolidine (III), m.p. 47.5—48.5° (vac.), $[\alpha]_D^{25} +59.9^\circ$ in EtOH. Equal amounts of (II) and (III) give (I), m.p. 53°. The hydrochlorides of (II) and (III) have m.p. 235—236°, $[\alpha]_D^{25} -24.8^\circ$ in H_2O , and m.p. 235—236°, $[\alpha]_D^{25} +25.3^\circ$ in H_2O , respectively. The *picrates*, m.p. 193—194° (decomp.), and *picrolonates*, m.p. 235.5—236° (decomp.), of (II) and (III) are described. The optically active products are not racemised extensively when heated with 5% HCl at about 90° or similarly with 5% KOH or alone at 150°/0.01 mm. Oxidation of (I) with KMnO_4 gives *m*-hemipinic acid, identified as the ethylimide. CH_2O and anhyd. HCO_2H convert (III) into non-cryst. *d*-carnegine, b.p. 100° (bath)/0.01 mm., $[\alpha]_D^{25} +24.6^\circ$ in EtOH. *l*-Carnegine has $[\alpha]_D^{25} -24.4^\circ$ in EtOH. The *picrates* and *picrolonates* of the active bases have m.p. 222° (decomp. in open tube) and m.p. 205—206°, respectively. H. W.

Ergot alkaloids. XIII. Precursors of pyruvic and isobutyrylformic acids. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1938, 122, 419—423).—Ergotinine is hydrogenated (Adams-Shriner PtO_2 in AcOH at 3 atm.) to a product which with KOH-MeOH yields isobutyrylformic acid (I), further hydrogenated in EtOH to α -hydroxyvaleric acid, which is not, however, detected in the former hydrogenation. Ergotamine similarly hydrogenated gives no nitroprusside reaction of AcCO_2H until the product is hydrolysed. It is suggested that the precursors of (I) and AcCO_2H from regotinine-ergotoxine (II)



and from ergotamine-ergotaminine (III) are $\text{OH} \cdot \text{CPr}^{\beta}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ and $\text{OH} \cdot \text{CMe}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, respectively, and that the formula represents (II) ($\text{R} = \text{Pr}^{\beta}$) and (III) ($\text{R} = \text{Me}$). E. W. W.

Microscopical examination of ergot alkaloids. III. Ergosine and ergosinine (ergoclavine). A. KOFLER (Arch. Pharm., 1938, 276, 40—45; cf. A., 1937, II, 393).—The crystallo-optical properties of ergosine, m.p. 208—212° (micro), and ergosinine, anhyd., m.p. 210—215°, and +MeOH, m.p. 190—192° or 210—215° (micro), are described. R. S. C.

Modified cinchona alkaloids. V. β -isoQuinotoxine and the stereochemistry of the parent bases. W. SOLOMON (J.C.S., 1938, 6—8).— β -iso-Quinotoxine has $[\alpha]_D^{25} -33.8^\circ$ in 0.1N- H_2SO_4 [*H* tartrate, m.p. 192—194° (decomp.), $[\alpha]_D^{25} -12.0^\circ$ in

H₂O; neutral tartrate (+2H₂O), m.p. 162—166° (decomp.), $[\alpha]_D^{25} -12.0^\circ$ in H₂O; sulphate (+3.5H₂O), m.p. 198—199° (decomp.), $[\alpha]_D^{25} -25.2^\circ$ in H₂O]. The evidence is thus in favour of the *l*-enantiomer configuration of the fourth C of the cinchona alkaloid mol.

F. R. S.

Cinchona and other alkaloids in bird malaria.

III. G. A. H. BUTTLE, T. A. HENRY, W. SOLOMON, J. W. TREVAN, and E. M. GIBBS (Biochem. J., 1938, **32**, 47—58).—See A., 1938, III, 224. The following are described: *ethers of apoquinine*: *Pr*^a, $[\alpha]_D^{25} -286.8^\circ$ [hydrochloride, m.p. 249—251° (decomp.), $[\alpha]_D^{25} -172^\circ$], *Pr*^β, $[\alpha]_D^{25} -288^\circ$ [hydrochloride, m.p. 254—257° (decomp.)], *Bu*^a, m.p. 162—164°, $[\alpha]_D^{25} -280.7^\circ$ [hydrochloride, m.p. 219° (decomp.)], *n*-amyl, m.p. 143—145.5°, $[\alpha]_D^{25} -268.1^\circ$ [hydrochloride, m.p. 234.5—236.5° (decomp.)], isoamyl, m.p. 185°, $[\alpha]_D^{25} -269.7^\circ$ (hydrochloride, m.p. 201—205°), *n*-hexyl, m.p. 135—137°, $[\alpha]_D^{25} -273.5^\circ$ in 0.1N-EtSO₃H (hydrochloride, m.p. 223—225°), *n*-heptyl, m.p. 137—140°, $[\alpha]_D^{25} -263.5^\circ$ in 0.1N-EtSO₃H (hydrochloride, m.p. 172—176°), *n*-octyl, m.p. 141—143°, $[\alpha]_D^{25} -232.5^\circ$ in 0.1N-EtSO₃H (hydrochloride, m.p. 90—145°), *sec*-octyl, $[\alpha]_D^{25} -225.6^\circ$ in 0.1N-EtSO₃H (*H* oxalate, decomp. 120°), *n*-nonyl, m.p. 138—141°, $[\alpha]_D^{25} -211.6^\circ$ in 0.1N-EtSO₃H (hydrochloride, m.p. 100—120°), *n*-decyl, m.p. 124—127°, $[\alpha]_D^{25} -177.6^\circ$ in 0.1N-EtSO₃H (hydrochloride, m.p. 90—115°), *n*-undecyl, m.p. 124—129°, $[\alpha]_D^{25} -164.6^\circ$ in 0.1N-EtSO₃H (hydrochloride, m.p. 100—120°), *cetyl*, m.p. 103—106°, $[\alpha]_D^{25} -132.7^\circ$ in 0.1N-EtSO₃H (hydrochloride, m.p. 90—110°). *Ethers of isoapoquinidine*: *Et* [sulphate, m.p. 140—145 (anhyd.), $[\alpha]_D^{25} -43.4^\circ$], *n*-amyl (*H* sulphate, m.p. 173°, $[\alpha]_D^{25} +26.2^\circ$), isoamyl [sulphate, m.p. 130° (decomp.), $[\alpha]_D^{25} +31.7^\circ$ in 0.1N-H₂SO₄], *n*-hexyl (*H* sulphate, m.p. 175°, $[\alpha]_D^{25} +24.9^\circ$ in 0.1N-HCl), *n*-heptyl (*H* sulphate, m.p. 170°, $[\alpha]_D^{25} +25.3^\circ$ in 0.1N-HCl), *n*-octyl (*H* sulphate, m.p. 161°, $[\alpha]_D^{25} -5.1^\circ$ in 0.1N-HCl). *Ethers of dihydrocupreine*: *Pr*^β, $[\alpha]_D^{25} -226^\circ$ (hydrochloride, m.p. 227—230°), *n*-amyl, m.p. 130—132°, $[\alpha]_D^{25} -210.2^\circ$ [dihydrochloride, m.p. 240—243 (decomp.)], $[\alpha]_D^{25} -177.9^\circ$, *n*-heptyl, m.p. 130—132°, $[\alpha]_D^{25} -198.9^\circ$ in 0.1N-EtSO₃H (dihydrochloride, m.p. 140—160°), *n*-octyl, m.p. 119°, $[\alpha]_D^{25} -186.3^\circ$ in 0.1N-EtSO₃H, *n*-nonyl, m.p. 130°, $[\alpha]_D^{25} -146^\circ$ in 0.1N-EtSO₃H (dihydrochloride, m.p. 180°), *n*-decyl, m.p. 111—113°, $[\alpha]_D^{25} -120.8^\circ$ in 0.1N-EtSO₃H (dihydrochloride, m.p. 135—155°), *undecyl*, m.p. 107—109°, $[\alpha]_D^{25} -108.7^\circ$ in 0.1N-EtSO₃H (dihydrochloride, m.p. 130—150°).

J. N. A.

Alkaloids from the bark of *Strychnos henningii*. III. Isolation of a second crystalline alkaloid. M. M. RINDL and M. L. SAPIRO (Trans. Roy. Soc. S. Africa, 1936, **23**, 361—365).—The bark of *S. henningii* contains 5—6% of a mixture of alkaloids. The cryst. alkaloid previously isolated is probably C₂₂H₂₅O₄N₂·OMe. A second alkaloid C₂₂H₂₄O₃N₂(OMe)₂, m.p. 214.5—215.0°, subliming at 190—200°/0.03 mm., gives colour reactions with Froehde's reagent similar to those of colubrine (cf. A., 1931, 1312).

H. J. E.

Atisan from *Aconitum heterophyllum*, Wall, and anthonin from *Aconitum anthora*. A. GORIS (Compt. rend., 1937, **205**, 1007—1009).—*A. heterophyllum* contains atisan (I), an isomeride (isoatisan)

(II) (hydrochloride, m.p. 331.5°, $[\alpha]_D^{25} +10.62^\circ$; hydroiodide, m.p. 272°), and an alkaloid insol. in Et₂O. *A. anthora* yields anthonin (identical with atisan) and *ψ*-anthonin. Jowett's artisan (J.C.S., 1896, **69**, 1518) is a mixture of (I) and (II).

J. D. R.

Influence of substitution in the nucleus on the reduction potential, the dissociation constants, and the surface activity of phenylarsinic acid. B. BREYER (Ber., 1938, **71**, [B], 163—171).—Determination of the reduction potentials of PhAsO₃H₂ and its 4-Me, 4-NHAc-, 4-OMe-, 2:4-Cl₂-, 4-OH- and 4-NH₂-derivatives by the polarographic method of Heyrovsky and Shikata shows that the influence of the substituents corresponds with the sequence: Me < NHAc < OMe < 2Cl < OH < NH₂. NO₂·C₆H₄·AsO₃H₂ cannot be investigated by this method since reduction first affects ·NO₂. It is remarkable that the introduction of Cl into the aromatic nucleus increases the difficulty of reducing PhAsO₃H₂. Generally the halogens as substituents appear to exert a somewhat uncertain influence. Anti-auxochrome action appears to predominate with Cl and to a smaller extent with Br, whereas I can reveal auxochrome activity. Determination of the dissociation consts. with the quinhydrone electrode places the negativising groups in the sequence NO₂ > Cl and the positivising groups in the order NHAc < Me < OMe < OH < NH₂. The surface activities of the acids and their derivatives are determined polarographically, the diminution of the O₂-max. being measured. If the val. of PhAsO₃H₂ is unity those of the Me, OH, NH₂, OMe, 2:4-Cl₂, and NHAc derivatives are 1.0, 1.5, 1.5, 3.0, 3.5, 8.5, and 22.2 respectively. It appears that the closing of the polar NH₂ or OH increase the surface activity in a degree >> calc. by the method of Bennett and Mitchell.

H. W.

o-Arsenated phenoxyalkanols. S. B. BINKLEY and C. S. HAMILTON (J. Amer. Chem. Soc., 1938, **60**, 134—135).—o-NO₂·C₆H₄·OK and CH₂Cl·CHMe·OH give β-o-nitrophenoxyisopropyl alcohol, b.p. 223—225°/25 mm., reduced (H₂-Raney Ni at 2 atm.) in MeOH to the NH₂-alcohol, m.p. 75°, which affords (Bart) β-o-arsinophenoxyisopropyl alcohol, m.p. 167° (Na salt). HNO₃ (d 1.5) converts this into β-4-nitro-2-arsinophenoxyisopropyl nitrate, m.p. 186°, hydrolysed by hot 3N-HCl to the NO₂-alcohol, m.p. 165—167°, which is hydrogenated to β-4-amino-2-arsinophenoxyisopropyl alcohol, +2H₂O and anhyd., m.p. 184° (Na salt). SO₂-HI reduces this base to 5-amino-2-β-hydroxy-n-propoxyphenylarsin oxide, amorphous, m.p. 125—128°, and 2-β-hydroxy-n-propoxyphenylarsin oxide, amorphous, m.p. 115—120°, and the 5-NO₂-derivative, amorphous, m.p. 152—154°, thereof are similarly obtained. Reduction by H₃PO₂ gives 2:2'-di-β-hydroxy-n-propoxyarsenobenzene, m.p. 121—124°. Attempts to oxidise the CH·OH to CO and to condense o-OH·C₆H₄·AsO₃H₂ with CH₂Cl·CHMe·OH failed.

R. S. C.

Organic arsenic compounds.—See B., 1938, 227.

Isomorphous relationships of some analogous organic derivatives of oxygen, sulphur, and selenium. N. M. CULLINANE and C. A. J. PLUMMER (J.C.S., 1938, 63—67).—The results of observ-

ations of temp.-concn. diagrams of binary mixtures of (a) diphenylene oxide (I), sulphide (II), and selenide (III), and (b) diphenylene dioxide (IV), disulphide (V), and diselenide (VI), are in harmony with the periodic relationships of the elements O, S, and Se. In series (a), (II) and (III) and (I) and (II) yield continuous series of solid solutions, whilst (I) and (III) exhibit only partial solid solubility. The system (V)-(VI) shows that an unbroken series of solid solutions is present, whereas the systems (IV)-(V) and (IV)-(VI) exhibit eutectics with negligible solid solution formation. The spatial configurations of the mols. are discussed in the light of the results. F. R. S.

resolved through the *nor-d-ψ-ephedrine* salt, m.p. 180°, $[\alpha]_{D}^{20} +16.7^\circ$ to $+17.4^\circ$ in aq. MeOH. The non-resolvability of the compounds is discussed. Selenanthren has a folded structure.

VII. 2-Aminophenoxtellurine could not be resolved through the *H. d-tartrate*, m.p. 158—159° (decomp.), $[\alpha]_{D}^{20} +2.45^\circ$ in EtOH, or *d-camphorsulphonate*, m.p. 182—185° (decomp.), $[\alpha]_{D}^{20} +14.0^\circ$ to 15.6° in EtOH. 4-Chloro-4'-methyl-diphenyl ether and TeCl_4 when heated together give a poor yield of a dichloride, reduced to 2-chloro-8-methylphenoxtellurine, m.p. 67—68°. 2-Amino-4'-methyl-diphenyl ether, diazotised and treated with HgCl_2 and then Cu at low temp., gives 2-chloromercuri-4'-methyl-diphenyl ether, m.p. 140°, which with TeCl_4 forms 4'-methyl-diphenyl ether 2-telluritrichloride, m.p. 180—185° (decomp.), converted by heating into 2-methylphenoxtellurine 10:10-dichloride, m.p. 274—275°. The dichloride is reduced to 2-methylphenoxtellurine, m.p. 50—52°, which could not be oxidised. A similar series of reactions with 2-amino-4'-carboxydiphenyl ether gives 2-chloromercuri-4'-carboxydiphenyl ether, m.p. 220° (decomp.), 4'-carboxydiphenyl ether 2-telluritrichloride, m.p. 205—206° (decomp.), 2-carboxyphenoxtellurine 10:10-dichloride, m.p. 319°, and phenoxtellurine-2-carboxylic acid, m.p. 231—233°. This acid could not be resolved through the *nor-d-ψ-ephedrine* salt, m.p. 144—145°, also $(+3\text{H}_2\text{O})$, $[\alpha]_{D}^{20} +16.8^\circ$ in EtOH; *strychnine* salt, m.p. 198—200° (decomp.), $[\alpha]_{D}^{20} -14.5^\circ$ in CHCl_3 ; *quinine* salt, m.p. 211°, $[\alpha]_{D}^{20} -125.1^\circ$ in CHCl_3 ; *cinchonidine* salt, m.p. 206°, $[\alpha]_{D}^{20} -59.4^\circ$; *d-α-phenylethylamine* salt, m.p. 205°, $[\alpha]_{D}^{20} +3.80^\circ$ to 4.19° in MeOH; and *l-menthyl* ester, m.p. 123—125°, $[\alpha]_{D}^{20} -51.9^\circ$ to -52.2° in COMe_2 . It is probable that the phenoxtellurine mol., although folded, is flexible. F. R. S.

Recent progress in the chemistry of the proteins. P. RONDONI (Chim. e l'Ind., 1938, 16, 65—73).—A review.

Proteins and proteolytic enzymes.—See A, III, 148.

Micro-determination of carbon and hydrogen. A. ELEK (Ind. Eng. Chem. [Anal.], 1938, 10, 51—52).—Suggested improvements in the Pregl technique include the use of Ag gauze in place of Ag thread in the combustion train, an improved electric heater and absorption tubes, the use of pure O_2 from liquid air, and employment of two specially designed boats and capillary tubes in the analysis of easily subliming and volatile substances. F. N. W.

Micro-determination of carbon and hydrogen. E. J. SHTUBER and M. E. MAURIT (J. Gen. Chem. Russ., 1937, 7, 2523—2531).—Directions for conducting micro-determination of C and H by a modified Pregl procedure are given. R. T.

Weighing tube for volatile liquids in carbon-hydrogen and Dumas nitrogen semimicro-determinations. V. A. ALUISE (Ind. Eng. Chem. [Anal.], 1938, 10, 56).—Use of a U-shaped capillary tube, centrifuged after filling and prior to sealing, overcomes the necessity of using KClO_3 in the Pregl straight weighing tube. F. N. W.

Configuration of heterocyclic compounds.

VI. Examination of derivatives of selenoxanthone and phenoxselenine. (MISS) M. C. THOMPSON and E. E. TURNER. VII. Some derivatives of phenoxtellurine. (MISS) I. G. M. CAMPBELL and E. E. TURNER (J.C.S., 1938, 29—36, 37—42).—VI. 2-Selenocyano-4'-methyl-diphenyl ether, prepared by diazotising the corresponding 2- NH_2 -compound and adding KCNSe , could not be oxidised satisfactorily. 2-Acetamido-4'-methyl-diphenyl ether, m.p. 92°, is oxidised (KMnO_4) to the 4'-carboxy-compound, m.p. 211°, hydrolysed to 2-amino-4'-carboxydiphenyl ether, m.p. 137°. The diazotised acid and KCNSe give 2-selenocyano-4'-carboxydiphenyl ether, m.p. 178°, oxidised (HNO_3) to 4'-carboxydiphenyl ether 2-seleninic acid, m.p. 212° (decomp.), which (85% H_2SO_4 ; aq. $\text{K}_2\text{S}_2\text{O}_5$) gives phenoxselenine-2-carboxylic acid, m.p. 251° [dibromide, m.p. 214° (decomp.)]. This acid could not be resolved through the following salts: *cinchonidine*, m.p. 211°; *d-* and *l-α-phenylethylamine*, *l-base* salt, m.p. 207°, $[\alpha]_{D}^{20} -3.5^\circ$ in MeOH; *brucine* salt trihydrate, $[\alpha]_{D}^{20} -10.3^\circ$ to 6.2° in COMe_2 , giving inactive acids. Selenoxanthone-1-carboxylic acid could not be resolved through the *l-CHPhMe-NH_2* or *strychnine* salt, m.p. 240—243°, $[\alpha]_{D}^{20} +3.5^\circ$ in CHCl_3 . 2':4'-Dichloro-2-nitro-4-carboxydiphenyl ether, m.p. 207—209°, obtained from 2:4- $\text{C}_6\text{H}_3\text{Cl}_2\text{OH}$ and 3:4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{H}$, is reduced (aq. $\text{NH}_3\text{-FeSO}_4$) to the 2- NH_2 -compound, m.p. 199° (*Ac* derivative, m.p. 232°), the diazo-derivative of which with KCNSe gives the 2-selenocyano-derivative, m.p. 247—248° (decomp.). This compound is oxidised (HNO_3) to 2':4'-dichloro-4-carboxydiphenyl ether 2-seleninic acid, decomp. $>176^\circ$, which gives (H_2SO_4 ; $\text{K}_2\text{S}_2\text{O}_5$) 6:8-dichlorophenoxselenine-2-carboxylic acid, m.p. 309°, which could not be resolved through the *d-α-phenylethylamine* salt, m.p. 250—256°, $[\alpha]_{D}^{20} +4.2^\circ$ in EtOH. The acid with NaOH affords 5:5'-dicarboxy-2:2'-di-(2':4'-dichlorophenoxy)diphenyl diselenide ($+2\text{AcOH}$), m.p. 278° (decomp.). 2-Nitro-4-carboxy-3':5'-dimethyldiphenyl ether, m.p. 179—181°, prepared from *m*-xylenol and 3:4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{H}$, is reduced to the 2- NH_2 -acid, m.p. 173° (*Ac* derivative, m.p. 219°), the diazo-derivative of which with KCNSe yields the 2-selenocyano-compound, m.p. 233° (decomp.). This substance with NaOH forms 5:5'-dicarboxy-2:2'-di-(4'-*m*-xylenoxy)diphenyl diselenide ($+2\text{AcOH}$), m.p. 239—243°. 2-Carboxyphenoxselenine 10-oxide, m.p. 217—218°, obtained by oxidation (H_2O_2) of the -carboxylic acid, could not be

Distillation of ammonia in Kjeldahl determinations with the Parnas-Wagner apparatus. J. K. PARNAS (*Acta Biol. Exp.*, 1937, **11**, 107—110).—Bartosiewicz's modification (*A.*, 1937, **II**, 129) is criticised.

R. T.

Micro-determination of phosphorus in organic compounds. E. I. AIZENSCHTADT (*Zavod. Lab.*, 1937, **6**, 1014—1016).—Minor modifications of Pregl's method are described.

R. T.

Titration with mixed indicators. A. ZIPEROVITSCH (*Ukrain. Biochem. J.*, 1937, **10**, 441—444).—CO₂H groups are determined using a 0.5% solution of mixed thymol- and phenol-phthaleins as indicator, whereby the colour change point is broader than with a single indicator.

P. G. M.

Application of the Raman effect to the analysis of organic mixtures. J. GOUBEAU (*Angew. Chem.*, 1938, **51**, 11—15).—The application of the Raman effect to qual. and quant. org. analysis is described. The sensitivity of the process is discussed. The method may be used (a) for testing the purity of a substance, (b) for identifying a substance (for which purpose it has several advantages over m.p. and b.p. determinations), (c) for analysing mixtures of many, or difficultly separable, constituents, *e.g.*, motor fuels, (d) the detection of classes of compounds. Quant. analysis depends on the determination of the intensity of the Raman lines.

A. J. M.

Cause of error in the determination of the diene value. S. SABETAY and Y. R. NAVES (*Bull. Soc. chim.*, 1937, [v], **4**, 2105—2107).—CH₂Ph·CH₂·OH, CH₂Ph·OH, *n*-C₈H₁₇·OH, geraniol, menthol, borneol, cholesterol, and ricin all react when heated with maleic anhydride. Thus the "diene val." of an oil or fat, determined by the method of Kaufmann (*A.*, 1936, 966) or of Sandermann (*B.*, 1937, 1370), may be quite misleading if alcohols are present.

E. W. W.

Determination of pentoses and other reducing sugars.—See *A.*, **III**, 162.

[Microchemical detection of acetic acid.]—See *A.*, **I**, 157.

Colour test for pentoses. H. TAUBER (*Proc. Soc. Exp. Biol. Med.*, 1937, **37**, 600—601).—1 g. of benzidine is dissolved in 25 c.c. of glacial AcOH. If 0.5 c.c. of this solution is added to one drop of a solution of arabinose, xylose, or ribose containing 0.05 mg. of the sugar, which is then boiled and cooled, a stable cherry-red colour develops.

V. J. W.

Biochemistry of carbohydrates. XXIX. Determination of non-amino-sugars by the Dische and Tillmans-Philippi methods. H. HISAMURA (*J. Biochem. Japan*, 1937, **26**, 359—372).—Tabulated data and curves indicate the accuracy obtainable in the colorimetric determination of non-amino-sugars (glycuronic acid, glucose, mannose, galactose, arabinose, xylose) at various concns. by

the orcinol method of Tillmans and Philippi (*Ozaki, A.*, 1937, **III**, 87) and the indole and phloroglucinol methods of Dische (*A.*, 1926, 1282). The reduction in colour due to mixing a sugar with either another sugar or an amino-sugar is indicated.

F. O. H.

Potentiometric determination of polypeptides and amino-acids. III. Titration of amino-acids and peptides in presence of sugars. E. W. BALSON and A. LAWSON (*Biochem. J.*, 1938, **32**, 230—234; cf. *A.*, 1936, 1006).—The changes in *p_H* observed when a sugar is added to a NH₂-acid buffer are due only to the acidic function of the sugar. The product of the reaction has an acid *K* not very different from that of the NH₂-acid itself. Hence the electrometric method cannot be used for studying the equilibrium. The *p_H* optimum curves obtained for CH₂O titration by Frankel and Katchalsky (*A.*, 1937, **II**, 402) are inconsistent with the accepted theory.

J. N. A.

Determination of adrenaline.—See *A.*, **III**, 162.

Determination of the phellandrenes by means of maleic anhydride. N. F. GOODWAY and T. F. WEST (*J.S.C.I.*, 1938, **57**, 37—38).—The maleic anhydride iodometric method (*A.*, 1937, **II**, 272, 296) for determining conjugated compounds is not applicable to β-phellandrene (I). Diene val. rose slowly to 31.8 in 10 hr., equiv. to 17% of (I), although the H₂ absorption corresponded with 77%. The diene val. of the α-phellandrene indicated 45% purity, H₂ absorption corresponding with 70%.

T. F. W.

Colour reaction of tannic acid. E. DURIO and M. GARINO (*Annali Chim. Appl.*, 1937, **27**, 523—525).—The application of the red colour given with aq. I and NaHCO₃ to the detection and determination of tannin (*e.g.*, in plant extracts) is described.

F. O. H.

Determination of histidine. R. J. BLOCK (*Proc. Soc. Exp. Biol. Med.*, 1937, **37**, 580—582).—Histidine is pptd. from the protein dialysate by AgNO₃ and the Ag is removed by H₂S. The histidine in solution can be determined colorimetrically as a Br-compound or gravimetrically as an insol. compound with nitranilic acid.

V. J. W.

Turbidimetric titration of small amounts of nicotine. L. D. GOODHUE (*Ind. Eng. Chem. [Anal.]*, 1938, **10**, 52—54).—A photo-electric apparatus including a special titration cell is used. 0.05—0.75 mg. of nicotine and 2 c.c. of silicotungstic acid solution (5 g. per l.) are pipetted into the cell and 4 drops of 1.5*N* aq. HCO₂H (to retard crystallisation), 4 drops of 2% aq. Irish moss extract (to prevent flocculation), and 10 c.c. of H₂O are added, and the mixture is titrated with standard aq. nicotine formate (0.5 g. per l.), the end-point being the point of max. turbidity, which is indicated photo-electrically.

F. N. W.

Titration constants of anserine, carnosine, and related compounds.—See *A.*, **I**, 144.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

APRIL, 1938.

Structure and properties of organic compounds. I. Structure and polar properties of molecules. II. Structure and acidic or basic properties of molecules. III. Energy of the linkings, and saturation of molecules. IV. High mol. wt. compounds. V. V. RAZUMOVSKI (J. Gen. Chem. Russ., 1937, 7, 2344—2355, 2356—2360, 2448—2456, 2626—2632).—Theoretical.

R. T.

Configurations about single linkings. A. WEISSBERGER (J. Org. Chem., 1937, 2, 245—252).—A review of the information obtained from dipole moment determinations about configurations around single linkings.

H. G. M.

Organic compounds with heavy hydrogen. F. ADICKES (Angew. Chem., 1938, 51, 89—93).—A review.

R. S. C.

System α -carbon tetrachloride-chlorine.—See A., 1938, I, 197.

$\beta\beta\gamma\delta$ -Tetramethylhexane and $\gamma\gamma\epsilon$ -trimethylheptane. N. L. DRAKE and L. H. WELSH (J. Amer. Chem. Soc., 1938, 60, 488—489).—The olefines obtained from $\text{CHMePr}^2\text{-OH}$ and H_2SO_4 are reduced by H_2 -Cu chromite at 270° , but not by Pt at room temp. Removal of olefines from the products by SiO_2 gel gives $\beta\beta\gamma\delta$ -tetramethylhexane, b.p. $156.6^\circ/763$ mm.; and $\gamma\gamma\epsilon$ -trimethylheptane, b.p. $159.2^\circ/763$ mm.

R. S. C.

Rate of ethylene polymerisation. F. R. RUSSELL and H. C. HOTTEL (Ind. Eng. Chem., 1938, 30, 183—189).—The rate of polymerisation of C_2H_4 in the gaseous phase differs little from the rate of polymerisation when dissolved in liquid C_{10}H_8 to the same concn., despite the presence in the latter case of 14 mols. of C_{10}H_8 per mol. of C_2H_4 . The polymerisation in its early stages is a second-order reaction in the gaseous phase whereas in the liquid phase (C_{10}H_8 as solvent) the reaction is between the second and third order. As reaction proceeds, the rate does not fall off, and it is concluded that secondary changes occur between C_2H_4 and its polymerides. No detectable reaction occurred between the C_{10}H_8 and the dissolved C_2H_4 . Addition of extra surface in the reaction bomb was without appreciable effect on the reaction, indicating the polymerisation reaction to be homogeneous. The effect of temp. on the primary reaction was to double the rate every 14.5° over the range 340 — 415° . The corr. energy of activation was 40,000 g.-cal. per mol. for the liquid-phase reaction, and 42,100 for the gas-phase reaction. H. C. M.

Reaction of sulphur dioxide with olefines. R. D. SNOW and F. E. FREY (Ind. Eng. Chem., 1938,

30, 176—182).—The reaction between SO_2 and olefines exhibits unusual chemical behaviour, light of <3000 A. or a catalyst being necessary. Several new catalysts which have prolonged activity and are effective in very low concn. are described; these include mild oxidising agents such as nitrates. Certain olefines, such as isobutene, which will itself react with SO_2 at a suitable low temp., inhibit the reaction of *n*-butene with SO_2 at room temp. The reaction exhibits an unusual temp. effect in that there exists a definite temp. apparently characteristic of the olefine, above which the reaction does not take place.

H. C. M.

Catalysts for the equilibrium, ethylene-water-ethanol. A. J. PAIK, S. SWANN, jun., and D. B. KEYES (Ind. Eng. Chem., 1938, 30, 173—175).—5% Ag_2SO_4 in H_2SO_4 on pumice was the best catalyst found for facilitating dehydration of EtOH at low temp., e.g., 170° , and atm. pressure. Ag_2SO_4 has no effect on the rate of attainment of equilibrium in the system $\text{EtOH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{EtHSO}_4 + \text{H}_2\text{O}$, but it greatly accelerates the rate of $\text{EtHSO}_4 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2\text{SO}_4$.

H. C. M.

Isomerisation of allene hydrocarbons in presence of silicates. VI. Isomeric transformations of C_4H_6 hydrocarbons. J. M. SLOBODIN (J. Gen. Chem. Russ., 1937, 7, 2376—2380).— CH:CEt yields chiefly $\text{CH}_2\text{:C:CHMe}$ (I), together with divinyl, when passed over floridin at 275° . CMe:CMe yields CH:CEt and (I) under similar conditions.

R. T.

Syntheses of $\alpha\epsilon$ -dimethylhexatriene, $\alpha\theta$ -dimethyloctatetraene, and $\alpha\mu$ -dimethyldodecahexaene. R. KUHN and C. GRÜNDMANN (Ber., 1938, 71, [B], 442—447).—Treatment of sorbaldehyde with MgEtBr gives $\Delta^{8,9}$ -octadien- ζ -ol, b.p. 74 — $75^\circ/12$ mm., converted by distillation with $p\text{-C}_6\text{H}_4\text{MeSO}_3\text{H}$ into $\Delta^{8,9}$ -octatriene ($\alpha\epsilon$ -dimethylhexatriene), m.p. 52° , which can be kept indefinitely in a vac. Similarly octatrienal yields $\Delta^{8,9}$ -decatrien- θ -ol, b.p. 93 — $98^\circ/0.6$ mm., apparently a mixture of stereoisomerides; it rapidly becomes autoxidised and polymerised by air, does not give a colour with SbCl_3 in CHCl_3 , and is rapidly carbonised by conc. H_2SO_4 . Dehydration of it, best with $p\text{-C}_6\text{H}_4\text{MeSO}_3\text{H}$ in Et_2O , affords $\Delta^{8,9}$ -decatetraene, m.p. 125° , which is very sensitive to air and becomes polymerised so readily that it cannot be kept unchanged in a high vac. It gives a raspberry-red colour with SbCl_3 in CHCl_3 . It gives 2 mols. of AcOH when oxidised by CrO_3 . Reaction with H_2 ceases after absorption of 2.6—2.8 mols. so that even the mildest catalysts appear to accelerate polymerisation more rapidly than hydrogenation. It is unchanged by maleic anhydride or $(\text{C:CO}_2\text{Me})_2$.

in boiling PhMe. $\Delta^{8,10}$ -Tetradecapentaen- μ -ol, m.p. 157°, from dodecapentaenal, is sufficiently stable to permit sublimation in a high vac. It gives a blue-violet solution with SbCl_3 in CHCl_3 and a pure blue colour in 100% HCO_2H . Dehydration of it by $p\text{-C}_6\text{H}_4\text{MeSO}_3\text{H}$ in boiling dioxan yields $\Delta^{8,10,14}$ -tetradecaheptaene, m.p. 205°, the first coloured, purely aliphatic hydrocarbon obtained synthetically. It gives an indigo-blue solution with SbCl_3 in CHCl_3 , but is not halochromic in 100% HCO_2H . H. W.

Spontaneous isomerisation of lycopene. L. ZECHMEISTER and P. TUZSON (Nature, 1938, 141, 249—250).—When chromatographically adsorbed on $\text{Ca}(\text{OH})_2$ lycopene sometimes shows an additional brown band, which is attributed to a new polyene, "neolycopene." Its formation in C_6H_6 or light petroleum is due probably to isomerisation at room temp., which is accelerated to an equilibrium val. on heating. L. S. T.

Isomeric transformations, and polymerisation of highly unsaturated hydrocarbons and their derivatives. A. E. FAVORSKI (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 979—1000).—Isomerisation of acetylenic hydrocarbons when these are heated with NaOH in EtOH is the result of intramol. rearrangements, involving migration of one or more H from one to the next or next but one C; this migration most often takes place from the β - to the α -C, but it may also take place to or from the α - or γ -C. The products thus formed are in many cases highly reactive (e.g., $\text{CH}_2\text{CH} \rightarrow \text{CH}_2\text{C}^{\cdot}$) and combine to yield polymerides or cyclic products. R. T.

Reactivity of organic compounds. N. D. CHERONIS (J. Chem. Educ., 1937, 14, 480—484).—Experiments suitable for demonstrating the different rates of hydrolysis of monohalogen compounds, and of oxidation of monohydroxy-compounds and hydrocarbons are described. L. S. T.

Peroxide effect in the addition of reagents to unsaturated compounds. XV. Addition of hydrogen bromide to α - and β -bromo- and -chloro-propenes. M. S. KHARASCH, H. ENGELMANN, and F. R. MAYO (J. Org. Chem., 1937, 2, 288—302, 400).— CMe_2Br_2 , the normal product of the addition of HBr to $\text{CMeBr}:\text{CH}_2$, is formed in a vac. in presence of antioxidants but the change is not particularly sensitive to small quantities of peroxides. In the presence of ascaridole 80—90% of $\text{CH}_2\text{Br}:\text{CHMeBr}$ is readily obtained. In the presence of air or of antioxidants in a vac. $\text{CMeCl}:\text{CH}_2$ gives CMe_2ClBr ; in the presence of an org. peroxide the main product is $\text{CH}_2\text{Br}:\text{CHMeCl}$. Even the "normal" addition of HBr is comparatively rapid and is complete within 1—2 days. In the presence of air and/or added peroxides $\text{CHCl}:\text{CHMe}$ adds HBr rapidly, giving $\text{CH}_2\text{Cl}:\text{CHMeBr}$ exclusively. In absence of air the same product is more slowly produced. Under very strict "antioxidant" conditions addition is very slow and the product is 66% of $\text{CH}_2\text{Cl}:\text{CHMeBr}$ and 33% of CHEtClBr . Nearly the same mixture can be obtained more rapidly if substances known to accelerate "normal" addition of HBr (e.g., AcOH or *tert*-butylcarbimide) are added. The use of EtSH as

solvent and antioxidant gives accelerated addition and more CHEtClBr but the change is complicated by side reactions. It appears that the "peroxide-catalysed" addition of HBr to $\text{CHCl}:\text{CHMe}$ yields exclusively $\text{CH}_2\text{Cl}:\text{CHMeBr}$ and that "normal" addition gives CHEtClBr . The "normal" addition, however, is so slow that the other type of reaction cannot be completely excluded. HCl , with which a peroxide effect has never been observed, does not add to $\text{CHCl}:\text{CHMe}$ at an appreciable rate at room temp. In presence of FeCl_3 the change takes place rapidly at 0° apparently with exclusive formation of CHEtCl_2 and it is justifiable to consider FeCl_3 as an accelerator of "normal" addition. In the absence of air and presence of FeCl_3 at 0° $\text{CHBr}:\text{CHMe}$ rapidly yields 33% of CHEtBr_2 and 66% of $\text{CH}_2\text{Br}:\text{CHMeBr}$. In a vac. and in the presence of antioxidants up to 8% of CHEtBr_2 is obtained in the presence of accelerators. Under all other conditions the only additive product obtained is $\text{CH}_2\text{Br}:\text{CHMeBr}$. There is no evidence that "normal" addition of HBr to $\text{CHBr}:\text{CHMe}$ gives more CHEtBr_2 than is obtained in the presence of FeCl_3 and, in support, it is found that the addition of HCl to $\text{CHBr}:\text{CHMe}$ in presence of FeCl_3 at 0° gives CHEtClBr and $\text{CH}_2\text{Br}:\text{CHMeCl}$ in the approx. ratio 1 : 2. In a discussion of the mechanism of the peroxide effect it is claimed that the essential feature of the addition of HBr under "antioxidant" conditions is that Br^{\cdot} is directed to the C atoms with lowest electron density and that under "peroxide" conditions the Br is directed towards the C with the greater electron density, giving a free radical which reacts with HBr giving a saturated compound and another Br which is responsible for the propagation of the chain reaction. The function of peroxides or O_2 is therefore to initiate a chain reaction which supplies Br atoms. The absence of a "peroxide" effect in the addition of HCl or H_2SO_4 to unsaturated mols. is readily understood. H. W.

Catalysis, the chemistry of the future.—See A., 1938, I, 204.

Dehydrogenation of methyl alcohol to form-aldehyde.—See A., 1938, I, 205.

Action of bromine on dry sodium ethoxide. I. S. P. LAGEREV (J. Gen. Chem. Russ., 1937, 7, 2381—2382).— NaOEt and Br afford a variety of products, of which Ac_2 , EtOH , and NaBr were identified.

R. T.

Odorous principle of matsutake (*Armillaria Matsutake*, Ito et Imai). II. S. MURAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 155—172).—The constituent of this plant giving a red *p*-nitrophenylhydrazone (A., 1937, III, 107) is furfuraldehyde. Matsutake alcohol (I) (modified prep.) is shown by degradation and synthesis to be 1- Δ^8 -*n*-octen- γ -ol (the H_2 -derivative is also synthesised) and by prep. of derivatives to be identical with the octenol from the needles of Arisan Hinoki (Kafuku et al., B., 1931, 565). *sec*- C_8 alcohols taste sweet only if they contain *n*- $\text{R}:\text{CH}(\text{OH})\text{C}^{\cdot}\text{CH}$. Ozonisation of (I) gives HCO_2H and α -hydroxy-*n*-heptaldehyde, an oil, converted by Ag_2O into *n*-hexoic acid (*p*-bromophenacyl ester, m.p. 72.5—72.8°), and 1- α -hydroxy-*n*-heptoic acid (II), b.p. 100—110°/8 mm. [*p*-bromo-

phenacyl ester (III), m.p. 92—93°, with a small amount of an acid (impure *p*-bromophenacyl ester, m.p. 125—127°), possibly $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, derived from Δ^7 -*n*-octen- α -ol. The *p*-bromophenacyl ester, m.p. 95°, of the *dl*-form of (II) does not depress the m.p. of (II). The *p*-bromophenacyl esters of *l*- and *dl*- $\text{CHMeEt}\cdot\text{CO}_2\text{H}$ have m.p. 55° alone or when mixed. $n\text{-C}_5\text{H}_{11}\cdot\text{MgBr}$ and $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$ give *dl*- Δ^4 -*n*-octen- γ -ol, b.p. 71°/12 mm. (4'-iododiphenylurethane, m.p. 135—136°), resolved by the strychnine salt of the *H* phthalate into *l*- [= (I)] and *d*-forms, $[\alpha]_D^{25} -13.1^\circ$, $+10.7^\circ$ in abs. EtOH, -6.7° , $+5.7^\circ$ in CHCl_3 . ζ -Methyl- Δ^4 -hepten- γ -ol, b.p. 64—65°/13 mm. (from *iso*- $\text{C}_5\text{H}_{11}\cdot\text{MgBr}$ and $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$), and Δ^4 -*n*-hepten- γ -ol, b.p. 55—56°/12 mm., give 4'-iododiphenylurethanes, m.p. 145.5—146.5° and 146—147°, respectively. R. S. C.

Hydrogenation of acetylene derivatives.
XXIX. Action of sodium and alcohol on acetylene glycols, and the geometrical isomerides of tetramethylbutenediol. J. S. SALKIND and S. V. BUCHOVETZ (J. Gen. Chem. Russ., 1937, 7, 2417—2422).—Di- and tetra-phenylbutenediol are recovered unchanged when boiled with a solution of Na in EtOH; in *iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$ the products are C_2H_2 and PhCHO or $\text{CHPh}_2\cdot\text{OH}$. $(\text{OH}\cdot\text{CMe}_2\cdot\text{C})_2$ (I) and NaOMe in MeOH yield an isomeride (II) (probably a polymorph) of (I), m.p. 101—102°, identical with Bourguet's "*trans*(γ)- $\beta\epsilon$ -dimethyl- Δ^7 -hexene- $\beta\epsilon$ -diol" (A., 1928, 989). (I) also isomerises to (II) when fused with it; the reverse change could not be effected. Salkind's *trans*(α)- $(\text{OH}\cdot\text{CMe}_2\cdot\text{CH})_2$ (III), m.p. 76—77° (A., 1923, i, 176), is not, as Bourguet stated, a mixture of (II) with the *cis*-form. Hydrogenation of (II) gives $(\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2)_2$ (Pt catalyst), or (III) (Pd catalyst), identical with that obtained similarly from (I). (II) and Br in CHCl_3 afford a Br_2 -derivative, m.p. 128—129.5°. R. T.

Ether-like compounds. XIX. Influence of the substituents in a normal atomic chain on the reactivity. M. H. PALOMAA (Ber., 1938, 71, [B], 480—491).—The reactivity of compounds $\text{Y}\cdot[\text{CH}_2]_n\cdot\text{X}$ in which X and Y are reactive or reaction-influencing groups shows a pronounced relative min. when X and Y are separated by a certain distance. O in every type (OH , $\text{C}\cdot\text{O}\cdot\text{C}$, $\text{C}\cdot\text{O}$, CO_2H , $\text{CO}_2\text{Alk.}$) when in the β -position causes such a min. in the esterification of acids, hydrolysis by acids, alcoholysis of esters, hydrolysis of amides and cyanides, and alcoholysis of acid chlorides; its incidence appears largely independent of the solvent used. Comparison of compounds $\text{C}\cdots\text{CX}$ and $\text{C}\cdots\text{O}\cdots\text{CX}$ shows that in the case of the relative min. the affinity magnitudes are depressed by O in general and particularly by O at β . Other "affinity magnitudes" do not show a corresponding min. and are increased by introduction of O. Such are the velocity coeff. of the alkaline hydrolysis of esters, the electrolytic dissociation const. of acids, and the equilibrium const. of the acid hydrolysis of esters and of the esterification of acids. O in esters is operative whether in the acidic or alcoholic component. In extreme cases in which O is very close to the reactive group profound changes in chemical behaviour are observed. The influence of a double linking generally

differs from that of an O atom. Me as substituent sometimes exerts an action similar to that of coordinatively unsaturated atoms (O, Cl, S), the degree of action decreasing in the sequence $\text{C}\cdot\text{O}$; $\text{C}\cdot\text{O}\cdot\text{C}$, Me. The possibility of explaining the behaviour of coordinatively unsaturated atoms by the hypothesis of the formation of complex rings is fully discussed.

H. W.

Lipoid phosphoric acid esters. A. GRÜN (Stiasny Festschr., 1937, 88—98).—Details are given of the prep. of *cetyl H₂ phosphate* and $\text{C}_{16}\text{H}_{33}\cdot\text{O}\cdot\text{PO}(\text{Cl})\cdot\text{OH}$ or $[\text{C}_{16}\text{H}_{33}\cdot\text{O}\cdot\text{PO}(\text{Cl})]_2\text{O}$ by the action of POCl_3 on *cetyl alcohol* (I). $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ and POCl_3 give *chloroethoxyphosphoryl chloride* (II), b.p. 96—104°/0.8—0.2 mm. *Chloroethyl cetyl H phosphate* is obtained from (I) and (II) followed by Ag_2O . *Chloroethyl octadecyl H phosphate* is obtained similarly. The compound, $\text{Me}\cdot[\text{CH}_2]_7\cdot\text{C}\cdot\text{C}\cdot[\text{CH}_2]_7\cdot\text{CO}\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{O}\cdot\text{PO}[\text{O}\cdot\text{NMe}_3])$, $\text{C}_2\text{H}_4\cdot[\text{OH}]_2\cdot\text{O}\cdot\text{P}(\text{O})\cdot\text{O}\cdot\text{C}_2\text{H}_4$, from stearolic diglyceride, P_2O_5 , and choline H carbonate, is described. D. B.

Hydrolysis of α - and β -glycerophosphates.—See A., 1938, III, 238.

Reflux condenser for the preparation of esters. ANON. (Synth. Org. Chem., 1938, 11, No. 1, 4).—A modification of the Clarke and Rahrs column for the continuous removal of, e.g., aq. C_6H_6 from a reaction mixture is described. S. M.

Reactions of ortho-esters with certain acid anhydrides. H. W. POST and E. R. ERICKSON (J. Org. Chem., 1937, 2, 260—266).— $\text{CH}(\text{OEt})_3$ does not react with keten. With Ac_2O at 22° in the dark it slowly gives an equilibrium in which about 41% of *diethoxymethyl acetate* (I), b.p. 79—80°/24 mm., 170—172°/743 mm., is present. This is converted by cold 5% NaOH into NaOAc , HCO_2Et , and EtOH and by cold 15% NaHCO_3 into NaOAc , HCO_2Et , EtOH, and CO_2 . It is rapidly hydrolysed by cold dil. acids and with NH_4Ph yields $\text{CH}(\text{NHPH})_3$, m.p. 137—138° (corr.). Et α -ethoxymethyleneacetate, b.p. 146°/11 mm., is formed from a gently boiling mixture of (I) and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$. The function of Ac_2O in the reaction between $\text{CH}(\text{OEt})_3$ and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ is not to remove EtOH but to give (I) which acts as an intermediate. Similarly $\text{CH}(\text{OEt})_3$ and $(\text{EtCO})_2\text{O}$ give *diethoxymethyl propionate*, b.p. 70—72°/10 m.m., 177—179°/751 mm. Evidence of the production of *diethoxymethyl butyrate* from $\text{CH}(\text{OEt})_3$ and $(\text{Pr}^i\text{CO})_2\text{O}$ is obtained but the compound has not been isolated. $\text{CMe}(\text{OEt})_3$ and Ac_2O appear to yield $\alpha\alpha$ -diethoxyethyl acetate (II), which could not be isolated. On distillation there are obtained large amounts of EtOAc and a fraction, b.p. 65—80°/16 mm., which rapidly becomes discoloured when kept. This yields EtOAc , a trace of AcOH , and α -ethoxyvinyl acetate (III), b.p. 130—133°, probably derived from (II) by loss of EtOH. $\alpha\gamma\gamma$ -Triethoxy- Δ^4 -butenyl acetate, b.p. 87—88°/13 mm., m.p. 20—21°, probably obtained by loss of AcOH from (II) and (III), is described. H. W.

Electrolysis [of acetates] with flowing liquid.—See A., 1938, I, 205.

Aliphatic substitution and the Walden inversion. III. Comparison, using radioactive bromine, of rates of inversion and substitution in the reaction of bromide ions with α -bromopropionic acid. W. A. COWDREY, E. D. HUGHES, T. P. NEVELL, and C. L. WILSON (J.C.S., 1938, 209—211; cf. Hughes *et al.*, A., 1935, 1465; 1936, 1239; 1937, II, 363).—To determine the bimol. velocity coeff. for the exchange of active and inactive Br between active LiBr and *dl*-CHMeBr·CO₂H in COMe₂, the mixture is neutralised after a known time, evaporated, acidified, extracted with Et₂O, and the activity of the residual LiBr compared with its initial activity. That this is equal to the coeff. for racemisation of *d*-CHMeBr·CO₂H in presence of LiBr shows that substitution is accompanied by inversion.

A. LI.

C₄-Saccharinic acids. VIII. Reactions of pentaerythritol. Preparation of $\beta\beta'$ -di-iodoisobutyric acid and its hydrolysis to $\beta\beta'$ -dihydroxyisobutyric acid. J. W. E. GLATTFIELD and J. M. SCHNEIDER (J. Amer. Chem. Soc., 1938, 60, 415—418; cf. A., 1937, II, 228).—(CH₂Br)₂C(CH₂·OH)₂ is oxidised by KMnO₄ to $\beta\beta'$ -dibromo- α -hydroxymethylisobutyric acid, m.p. 146°, and with Na-EtOH in liquid NH₃ affords 25% of pentaerythritol Et₂ ether, b.p. 116°/5 mm., which is very readily oxidised. C(CH₂·OH)₄, Na, and EtBr in liquid NH₃ give much pentaerythritol Et₄, b.p. 83°/5 mm., with some of the Et₃, b.p. 94°/5 mm., and Et₂ ether. (CH₂Cl)₂C(OH)·CO₂H and HI at 100° give 20% of $\beta\beta'$ -di-iodoisobutyric acid (I), m.p. 128—130° (decomp.) (cf. Fischer *et al.*, A., 1889, 478), which with hot H₂O gives a solution probably containing (OH·CH₂)₂CH·CO₂H, since with HI it regenerates (I); however, evaporation gives increasing amounts of an insol. acid, which from analysis is probably a polymeride of hydroxymethylacrylic acid. R. S. C.

Oxidation of [methyl] sorbate with perbenzoic acid. P. HEINÄNEN (Suomen Kem., 1938, 11, B, 2—3).—Me·[CH(CH₃)₂]·CO₂Me with BzO₂H at 0° yields Me $\gamma\delta$ -oxido- Δ^{α} -hexenoate, b.p. 89°/10 mm., from which the free acid (I), m.p. 84—86°, and the explosive Ag salt have been prepared. Dil. HCl converts (I) into $\gamma\delta$ -dihydroxy- Δ^{α} -hexenoic acid, m.p. 68—77°, purified via the Ag salt. M. H. M. A.

Condensation of glycidic esters with malonic and acetoacetic esters. G. V. TSCHELINCEV and E. D. OSETOVA (J. Gen. Chem. Russ., 1937, 7, 2373—2375).— $\text{O} \begin{array}{c} \text{CMe}_2 \\ \diagup \quad \diagdown \end{array} \text{CH} \cdot \text{CO}_2\text{Et}$, NaOEt, and CH₂Ac·CO₂Et (I) in EtOH at 100° (13 hr.) yield Et α -acetyl- $\gamma\gamma$ -dimethylbutyrolactone- β -carboxylate, b.p. 150—152°/11 mm. Similarly $\text{O} \begin{array}{c} \text{CPh} \\ \diagup \quad \diagdown \end{array} \text{CH} \cdot \text{CO}_2\text{Et}$ with (I) gives Et α -acetyl- γ -phenylbutyrolactone- β -carboxylate, b.p. 162—165°/1 mm., and with CH₂(CO₂Et)₂ affords Et₂ γ -phenylbutyrolactone- $\alpha\beta$ -dicarboxylate, b.p. 225—227°/1 mm. R. T.

Cork. IX. Constitution of phloionic and phloionolic acid. F. ZETSCHE and K. WEBER (J. pr. Chem., 1938, [ii], 150, 140—144; cf. A., 1938, II, 25).—Phloionic acid (I) is [·CH(OH)·[CH₂]₇·CO₂H]₂,

since with Pb(OAc)₄ it gives only (82%) CHO·[CH₂]₇·CO₂H (II). Phloionolic acid (III) is OH·[CH₂]₈·[CH(OH)]₂·[CH₂]₇·CO₂H, since with Pb(OAc)₄ it gives (II) and a δ H-aldehyde (2:4-di-nitrophenylhydrazone, m.p. 67—67.5°), converted by Ag₂O into [CH₂]₇· $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$ ·O. Phellonic acid, (I), and (II) are optically inactive, but may have been racemised during isolation. R. S. C.

Derivatives of *d*- and *l*-erythronic acid. (Miss) V. C. JELINEK and F. W. UPSON (J. Amer. Chem. Soc., 1938, 60, 355—357).—*l*- and *d*-Erythronolactone and Ac₂O·HCl or BzCl at 100° give the Ac₂, a resin, [α]_D²⁵ +50.73°, —50.64° in 80% COMe₂, and Bz₂ derivatives, m.p. 110—111°, [α]_D²⁵ +176.29°, —176.86° in CHCl₃, respectively, and with liquid NH₃ afford *l*- and *d*-erythronamide, m.p. 91—92°, [α]_D²⁵ —26.22°, +26.23° in H₂O (Ac₃, brown resins, and Bz₂ derivatives, m.p. 201°, [α]_D²⁵ about +10°, —9° in CHCl₃). 63% pure *dl*-erythronic acid is obtained by Rehorst's method. Impure (I) gave *d*-threophenylhydrazide. R. S. C.

Action of ascorbic acid and dehydroascorbic acid on amino-acids. E. ABDERHALDEN (Fermentforsch., 1938, 15, 522—528; cf. A., 1937, II, 37).—Ascorbic (I) or dehydroascorbic acid in presence of O₂ and Fe⁺⁺⁺ converts NH₂-acids into the corresponding aldehydes having 1 C less, CO₂ and NH₃ being eliminated. Tyrosine probably yields 3:4-dihydroxyphenylacetaldehyde. The dimethylcyclohexanedione compounds of prop-, but-, isobut-, valer-, isovaler-, methylethylacet-, and phenylacet-aldehyde have m.p. 154—156°, 134—135°, 153—154°, 107—108°, 156—157°, 135—136°, and 165—166°, respectively. The extent of deamination of NH₂-acids by (I) + ultra-violet light is increased by Cu. W. McC.

Rotatory power of mixtures of ascorbic acid and sodium hydroxide. (MLLE.) S. GUINAND and J. NICOLLE (Compt. rend., 1938, 206, 105—107).—Aq. NaOH was added to aq. ascorbic acid containing a trace of quinol, and the rotatory power was determined for the yellow, green, and indigo lines of Hg. The curve of rotatory dispersion versus vol. of NaOH added rises rapidly to the equiv. point, and then more slowly. These results and those with variable content of ascorbic acid indicate that an acidity analogous to that of glucose appears in alkaline solutions, probably owing to the opening of the lactonoid structure OH·CH₂·CH(OH)·CH·C(OH):C(OH)·CO.

$$\text{O} \begin{array}{c} \diagup \quad \diagdown \\ \text{O} \end{array}$$
 R. S. B.

Preparation of acetylaldonic acids. C. D. HURD and J. C. SOWDEN (J. Amer. Chem. Soc., 1938, 60, 235—237).—A general method of converting aldoses into fully acetylated aldonic acids is described. Penta-acetyl-*d*-gluconitrile and *d*-galactonitrile, m.p. 136—137°, tetra-acetyl-*d*-xylo-nitrile, m.p. 79—81°, and *l*-arabonitrile, m.p. 118—120°, with HBr·AcOH give the corresponding amides, m.p. 187—187.5°, m.p. 166—167°, [α]_D²⁵ +27° in CHCl₃, m.p. 110.5—111.5°, [α]_D²⁵ +8° in CHCl₃, and m.p. 119—120°, [α]_D²⁵ —23° in CHCl₃, respectively, which with N₂O₃ in AcOH at 10—18° afford penta-acetyl-*d*-gluconic, penta-acetyl-*d*-galactonic, m.p. 131—132°, [α]_D²⁵ +12° in CHCl₃, and tetra-acetyl-*l*-arabonic acid,

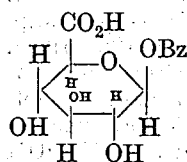
m.p. 135—135.5°, $[\alpha]_D^{25}$ -32° in CHCl_3 . The amides are unaffected by HNO_3 in AcOH or dil. mineral acid.

R. S. C.

Conversion of uronic acids into corresponding hexoses. IV. Catalytic reduction of the methyl ester of diisopropylidene-*d*-galacturonic acid. P. A. LEVENE and C. C. CHRISTMAN (J. Biol. Chem., 1938, 122, 661—664).—The *Me* ester, b.p. 133° (bath)/0.17 mm., $[\alpha]_D^{25}$ -93.4° in CHCl_3 , from diisopropylidene-*d*-galacturonic acid (A., 1934, 280) and CH_2N_2 , is reduced by H_2 (Cu chromite) to diisopropylidene-*d*-galactose, which is not hydrogenated further.

E. W. W.

Derivatives of glycuronic acid. VIII. Structure of benzoylglycuronic acid. W. F. GOEBEL (J. Biol. Chem., 1938, 122, 649—653).—(—)-Benzoylglycuronic acid (A., 1926, 1056) (Na salt, new $[\alpha]_D^{25}$ -27.7° in H_2O) must be a 1-Bz derivative, of the annexed formula, in agreement with Pryde and Williams (A., 1933, 1036; cf. A., 1934, 633), since its *Me* ester, new m.p. 190—191°, new $[\alpha]_D^{25}$ -16.3° in MeOH , gives an Ac_3 derivative, m.p. 145°, $[\alpha]_D^{25}$ -16.6° in CHCl_3 , identical with *Me* 1-benzoyl-2:3:4-triacetylglycuronate obtained from *Me* 1-bromo-2:3:4-triacetylglycuronate (A., 1935, 1483; 1936, 1231) and AgOBz .



E. W. W.

$\alpha\alpha'$ -Disulphidodipropionic acid. A. FREDGA (Arkiv Kemi, Min., Geol., 1937, 12, A, No. 13, 17 pp.).—*meso*-Di-(α -carboxyethyl) disulphide (I), m.p. 118—119°, k 7.3×10^{-4} (dibrucine, + about $6\text{H}_2\text{O}$, and distrychnine, + $5\text{H}_2\text{O}$, salts), is isolated as $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$ salt from the products from $\text{CHMeBr}\cdot\text{CO}_2\text{Na}$ and K_2S_2 . The *dl*-form (II), also obtained, had m.p. 148—149° and k 7×10^{-4} and was resolved by strychnine to give the *d*-, $[\alpha]_D^{25}$ +431.8° in 0.1N-HCl, +148.2° as Na salt (dibrucine salt, + $6.5\text{H}_2\text{O}$), and by $\text{NH}_2\cdot\text{CHPhMe}$ to give the *l*-form. An eutectic mixture, m.p. about 105°, of (I) and (II) contains about 32% of (II). Interconversion of (I) and (II) is rapid in alkali, slow in neutral and very slow in acid solution; it occurs by hydrolysis of R_2S_2 to $\text{RSH} + \text{RS}\cdot\text{OH}$, followed by oxidation of 2 RSH to R_2S_2 , a mechanism supported by unimol. reaction of *d*-(II) with $\text{dl-SH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$.

R. S. C.

Stereoisomeric forms of methylenedi- α -thiolpropionic acid. A. FREDGA (Arkiv Kemi, Min., Geol., 1937, 12, A, No. 15, 12 pp.).— $\text{SH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, CH_2O , and HCl give a mixture of *meso*-, m.p. 81.5—82.5° (diquinine salt, + $2\text{H}_2\text{O}$), and *dl*-methylenedi- α -thiolpropionic acid, m.p. 155—156°; the latter is best resolved by quinine in 45% aq. COMe_2 to give the *d*-(diquinine salt, + H_2O) and *l*-form, m.p. 82.5—83.5°, $[\alpha]_D^{25}$ -376.3° in 0.5N-HCl, -335.2° in 0.5 and -296.1° in 1 equiv. of NaOH , -556.5° in EtOH (diquinine salt, + $4\text{H}_2\text{O}$). Both acids have k 4.2×10^{-4} . The *meso*- and *l*-acids give a 1:1 mol. compound, m.p. 80.7°, the simplest known case of a partial racemate.

R. S. C.

Stereoisomeric α -alkylthiol- and -alkylsulphonyl-propionic acids. A. MELLANDER (Arkiv Kemi, Min., Geol., 1937, 12, A, No. 16, 32 pp.).—Pri

and $\text{SNa}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na}$ give α -n-, b.p. 127.8—128.8°/9 mm. (*Ag* and *Ba* salts), and *iso*-propylthiolpropionic acid, b.p. 120.8—121.4°/9 mm., m.p. 14.3—14.8° (*Ag*, + $0.5\text{H}_2\text{O}$, and *Ba* salts), and thence the *l*-n-propylthiol-, $[\alpha]_D^{25}$ -106°, $[\alpha]_{\text{H}_2\text{O}}^{25}$ -126° [quinine salt, + H_2O , m.p. (anhyd.) 92.5—94°], and *l*-[quinine salt, + H_2O , m.p. (anhyd.) 133.2—134.4°] and *d*-isopropylthiolacid, $[\alpha]_D^{25}$ +113.7°, $[\alpha]_{\text{H}_2\text{O}}^{25}$ +135.5° [brucine salt, + $2\text{H}_2\text{O}$, m.p. (anhyd.) 76—77.5°]. *d*-[quinidine salt, + $2\text{H}_2\text{O}$, m.p. (anhyd.) 66—67°] and *l*- α -Ethylthiolpropionic acid, $[\alpha]_D^{25}$ +111.8°, $[\alpha]_{\text{H}_2\text{O}}^{25}$ +132.6°, are prepared. Oxidation by KMnO_4 at p_{H} 6.98 (phosphate buffer) gives *dl*-, m.p. 59—60° (*Ag* and *Pb* salts; α -Br-derivative, m.p. 124.8—126°), and *l*- α -n-, $[\alpha]_D^{25}$ -36.8°, $[\alpha]_{\text{H}_2\text{O}}^{25}$ -44.2°, and *dl*-, m.p. 104.5—105.5° (*Ag* salt; α -Br-derivative, m.p. 63.6—65°), *l*- and *d*- α -iso-propylsulphonylpropionic acid, $[\alpha]_D^{25}$ +40.6°, $[\alpha]_{\text{H}_2\text{O}}^{25}$ +48.3°. The following data are also recorded: α -methyl-, m.p. 17.3°, b.p. 106.5°/9 mm., and -ethylthiolpropionic acid, b.p. 115.5°/9 mm.; *dl*-, m.p. 96.6° [α -Br-derivative, m.p. 173° (decomp.)], *l*- and *d*- α -methyl-, $[\alpha]_D^{25}$ +25° to 28°, *dl*-, m.p. 62.6° (α -Br-derivative, m.p. 96.5°), *l*- and *d*- α -ethylsulphonylpropionic acid, $[\alpha]_D^{25}$ +35.9°, $[\alpha]_{\text{H}_2\text{O}}^{25}$ +42.5°. The Br-acids react quantitatively, but slowly, with N_2H_4 to give $\text{AlkSO}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. *n*, *d*, and *k* are recorded. M.p. are corr. $[\alpha]$ are in H_2O ; they are almost unchanged in HCl , but are lower in NaOH .

R. S. C.

Stereoisomeric $\alpha\alpha'$ -dithioladipic acids. A. FREDGA (Ber., 1938, 71, [B], 289—295).—*meso*- $\alpha\alpha'$ -Dibromoadipic acid is converted into *meso*- $\alpha\alpha'$ -diethylxanthoadipic acid, m.p. 163.5—164.5°, transformed by conc. NH_3 - MeOH at room temp. into *meso*- $\alpha\alpha'$ -dithioladipic acid, m.p. 188° (slight decomp.), which can be titrated iodometrically or mercurimetrically, but alkalimetrically only under strictly defined conditions; it is oxidised by I or H_2O_2 to *meso*-1:2-dithian-3:6-dicarboxylic acid (I), $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$, m.p. 199°. *r*- $\alpha\alpha'$ -Diethylxanthoadipic acid, m.p. 131—132°, is transformed into *r*-1:2-dithian-3:6-dicarboxylic acid (II), m.p. about 275° (decomp.), also obtained in poor yield from *r*- $\alpha\alpha'$ -dibromoadipic acid and K_2S or (best) by isomerisation of (I) at 220°. It is reduced by Zn dust and NH_3 to *r*- $\alpha\alpha'$ -dithioladipic acid, m.p. 111.5—112.5°. (II) is resolved into its optical antipodes by quinidine in boiling COMe_2 , thus giving (+)-1:2-dithian-3:6-dicarboxylic acid (III), m.p. about 257°, $[\alpha]_D^{25}$ +336.6° in dil. Na_2CO_3 ; in org. media it is dextro- but in dil. HCl it is laevo-rotatory. Treatment of the mother-liquors from (III) with cinchonine leads to (—)-1:2-dithian-3:6-dicarboxylic acid (IV), m.p. about 257°, $[\alpha]_D^{25}$ -335.8° in dil. Na_2CO_3 . Reduction of (IV) by Zn dust- NH_3 affords (—)- $\alpha\alpha'$ -dithioladipic acid, m.p. 119.5—120.5°, $[\alpha]_D^{25}$ -59.2° in 0.4N-HCl. By interaction with the appropriate org. halide $[\text{CH}_2\cdot\text{CH}(\text{SR})\cdot\text{CO}_2\text{H}]_2$ is converted into the following derivatives, of which those belonging to the *meso* series have higher m.p. and smaller solubility than those belonging to the *r*-series. The m.p. are given in the sequence *meso*-*r*. $\text{R} = \text{Me}$, m.p. 193°, 124°; $\text{R} = \text{Et}$, m.p. 171°, 109.5°; $\text{R} = \text{C}_3\text{H}_5$, m.p. 121°, 102°; $\text{R} = \text{CH}_2\text{Ph}$, m.p. 169°, 130°; $\text{R} = 2:4\text{-C}_6\text{H}_3(\text{NO}_2)_2$,

m.p. about 275°, 230°; R = CH₂·CO₂H, m.p. 177°, 162·5°. The compounds $\left[\cdot \text{CH}_2 \cdot \text{CH} \begin{array}{c} \text{CO} \cdot \text{O} \\ \text{S} \end{array} \text{CMe}_2 \right]_2$, m.p. 138·5—139·5° and m.p. 102—103°, respectively, are obtained by condensing the *meso*- and *r*-acid with COMe₂ and HCl. H. W.

Behaviour of diselenodicarboxylic acids towards mercury salts. A. FREDGA (Ber., 1938, 71, [B], 286—289).—Addition of Hg salts to diselenodicarboxylic acids causes dismutation. In consequence of the presence of CO₂H the change is somewhat complicated but it can be schematically represented: 2RSe·SeR + 3HgCl₂ + 2H₂O ⇌ 2RSe·HgCl + R·SeO₂H + 3HCl. The reaction is completely reversible and the equilibrium is dependent on the H- and halogen-ion concn. (in consequence of complex formation between the latter and Hg). Other Hg^{II} salts appear to give similar results but the phenomena are complicated by the production of basic compounds. Complete reversibility is shown by the polarimetric titration with alkali of optically active (·Se·CHMe·CO₂H)₂ in presence of Br⁺ but partly with and partly without HgCl₂. In each case the solution is back-titrated with HCl. The two graphs are coincident until the CO₂H groups are nearly neutralised; in presence of Hg salt the dismutation then begins to become obvious and the graphs become separated from one another, becoming then re-united during back-titration and finally reaching the same activity. The measurements show that the dismutation equilibrium is reached almost instantaneously. In presence of an excess of I⁺ the Hg is in such firm complex union that dismutation is not complete even in moderately conc. solution of alkali. The acids employed are (·Se·CH₂·CO₂H)₂, (+)(·Se·CHMe·CO₂H)₂, (·Se·CH₂·CH₂·CO₂H)₂, (·Se·CHEt·CO₂H)₂, (·Se·CMe₂·CO₂H)₂, and diselenocyclotetramethylene-dicarboxylic acid. H. W.

Dimeride of crotonaldehyde. Hydrogenation of the corresponding acid and the transposition of its double linking with the aid of nickel. M. DELÉPINE and A. HOREAU (Compt. rend., 1938, 206, 27—29).—Oxidation of the dimeride of crotonaldehyde (cf. A., 1910, i, 219) affords an acid (I), reduced (H₂-Raney Ni) to 2:6-dimethyl-2:3-dihydro-1:4-pyran-5-carboxylic acid (II), m.p. 124° (J.C.S., 1914, 105, 1353), and its 5:6-H₂-derivative, m.p. 91°, and possibly some of the other possible stereoisomerides. (II) is also formed from the Na salt of (I) with Ni at room temp., or more readily at 100°. (II) is not reduced by H₂-Raney Ni at room temp. J. L. D.

Structure of polymerides: the polymeride from methyl vinyl ketone. C. S. MARVEL and C. L. LEVESQUE (J. Amer. Chem. Soc., 1938, 60, 280—284).—The polymeride obtained from COMe·CH·CH₂ and 0·5% of Bz₂O₂ at 50—60° is the head-to-tail substance, since it gives reactions of α-, but not of αδ-, diketones. It is unaffected by ZnCl₂ in dioxan at 50°, with SeO₂ gives the substance, [·CH₂·CH·CO·CHO]_n, and is pyrolysed at 270—360° to give 1 mol. of H₂O and a mixture containing 3-methyl-Δ²-cyclohexenone (2:4-dinitrophenylhydrazone, m.p. 172·5—173°; also pre-

pared from CHNaAc·CO₂Et and COMe·CH·CH₂), and the oxime does not give a compound of C₆H₅N type. R. S. C.

Action of magnesium *tert*-butyl chloride on ethyl heptoate and benzoate. A. D. PETROV, BELAEVA, and KUKANOVA (J. Gen. Chem. Russ., 1937, 7, 2665—2667).—Et heptoate in Et₂O and MgBu⁺Cl afford dihexyl ketone. EtOBz similarly yields CHPh₂·OH. R. T.

Action of the Oppenauer reagent on primary alcohols, including vitamin-A. J. W. BATTY, A. BURAWOY, S. H. HARPER, I. M. HEILBRON, and W. E. JONES (J.C.S., 1938, 175—179).—In an attempt to prepare the corresponding aldehyde, vitamin-A was heated with Al(OBu⁺)₃ in COMe₂-C₆H₆. The product, purified by Girard reagent P, was β-keto-μ-(2:2:6-trimethyl-Δ⁶-cyclohexenyl)-ζ-κ-dimethyl-Δ²-dodecapentaene, b.p. about 130°/10⁻⁴ mm. (semicarbazone, m.p. 193°; *p*-tolylsemicarbazone, m.p. 217—218°; *p*-chlorobenzoylhydrazone, m.p. 198—199°). With the same reagent geraniol or citral yields ψ-ionone, and cinnamyl, furfuryl, and benzyl alcohols yield condensation products with COMe₂, whereas tetrahydrogeraniol, Ph·[CH₂]₂·OH, and Ph·[CH₂]₃·OH are unaffected. In no case could the intermediate aldehyde be isolated. A. LI.

Acyloins. VIII. Racemisation and dimerisation of optically active acetoin. W. DIRSCHERL and A. SCHÖLLIG (Ber., 1938, 71, [B], 418—423).—When optically active acetoin is preserved an optically inactive cryst. dimeride (I) separates. At first [α] diminishes slowly with time but as pptn. occurs that of the still liquid portion increases gradually. The diminution is due to racemisation, the increase to the separation of the optically inactive dimeride. Racemisation and dimerisation are two distinct processes independent of one another. In addition to OH·CMe<CMe(OH)>CMe·OH the structure

O<CMe(OH)·CMe(OH)>O is possible for (I).

H. W.

Tetrose sugars. III. *l*-Threose and its derivatives. *d*-Lyxosediacetamide and *d*-arabinosedi-acetamide tetra-acetate. R. C. HOCKETT, V. DEULOFEU, A. L. SEDOR, and J. R. MENDIVE (J. Amer. Chem. Soc., 1938, 60, 278—280).—*l*-Xylonitrile tetra-acetate, m.p. 81—82°, [α]_D²⁰ -50·4°; *l*-, m.p. 165—167° (tri-acetate, m.p. 179°, [α]_D²⁰ -74°; benzylidene derivative, m.p. 265—266° after sintering at 260°, levorotatory), and *d*-threosediacetamide (tribenzoate, m.p. 155—156°, [α]_D²⁰ +109·7°; benzylidene derivative, m.p. 265° after sintering at 261°, dextro-rotatory), and *d*-lyxosediacetamide, m.p. 235—236°, are prepared. Hydrolysis of *d*-arabinosediacetamide tetra-acetate, m.p. 222—223° [α]_D²⁰ +72·5°, indicates [α]_D²⁰ -103·8° for *d*-arabinose. [α] are in C₂H₅Cl₃. M.p. are corr. Elimination of HCN from acetylated aldono-nitriles is better effected by aq. NH₃ than by NH₃-Ag₂O. R. S. C.

Esters of the aldehydrol form of sugars. II. M. L. WOLFROM and M. KONIGSBERG (J. Amer. Chem. Soc., 1938, 60, 288—289; cf. A., 1931, 1039).—

aldehydo-*l*-Arabinose tetra-acetate and AcBr at room temp. give aldehydo-*l*-bromo-*l*-arabinose penta-acetate, m.p. 130—131°, $[\alpha]_D^{25}$ -134° (const.) in CHCl_3 . Similar reactions give aldehydo-*l*-chloroarabinose penta-acetate, m.p. 109—110°, $[\alpha]_D^{25}$ -96° in CHCl_3 , -*l*-chloro-, m.p. 105—106°, $[\alpha]_D^{25}$ -49° in CHCl_3 , and -*l*-bromo-*d*-glucose hexa-acetate, m.p. 129—130°, $[\alpha]_D^{25}$ -79° in CHCl_3 . aldehydo-Galactose penta-acetate Et semi-acetal and Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 0° give aldehydo-*l*-ethoxy-*d*-galactose hexa-acetate, m.p. 97°, $[\alpha]_D^{25}$ +3.4° in CHCl_3 , +10° in EtOH, converted by $\text{HCl-Et}_2\text{O}$ into aldehydo-*l*-chloro-*l*-ethoxy-*d*-galactose penta-acetate, m.p. 142—143°, $[\alpha]_D^{25}$ -56° \rightarrow +25° in CHCl_3 .

R. S. C.

Identification of glucose. Acetolysis of glucosides. M. FRÈREJACQUE (Compt. rend., 1938, 206, 111—113).—Prolonged interaction of many glucosides (0.5—1 g.) with $\text{Ac}_2\text{O-H}_2\text{SO}_4$ at 40° affords glucose α -(I) and β -penta-acetate and the Ac derivative of the aglucone. The Et_2O -sol. portion of the mixture with $p\text{-C}_6\text{H}_4\text{Me-NH}_2$ in AcOH affords β -tetra-acetylglucosidyl-*p*-toluidide (II) (cf. A., 1936, 716). Hesperidoside and amygdalosite similarly treated afford (I). Mannose penta- and rhamnose tetra-acetate with $p\text{-C}_6\text{H}_4\text{Me-NH}_2$ afford products easily distinguished from (II) by their high solubility in EtOH.

J. L. D.

Unimolar *p*-toluenesulphonation of α - and β -methyl-*d*-glucosides. J. COMPTON (J. Amer. Chem. Soc., 1938, 60, 395—399).—New and known reactions suggest that the relative ease of acylation of different OH groups of sugars depends partly on the reagent. *iso*Propylidene-*d*-glucose 6-*p*-toluenesulphonate and 70% AcOH at 26—30° (7 days) give β -*d*-glucose 6-*p*-toluenesulphonate, m.p. 132—133°, $[\alpha]_D^{25}$ +21° \rightarrow +39° in 4 hr. in H_2O , the tetra-acetate, m.p. 203—204°, $[\alpha]_D^{25}$ +23.7° in CHCl_3 , of which with HBr-AcOH at 0° gives acetobromo-*d*-glucose 6-*p*-toluenesulphonate, m.p. 88—89°, $[\alpha]_D^{25}$ +166.1° in CHCl_3 , and thence by $\text{MeOH-Ag}_2\text{CO}_3$ β -methyl-*d*-glucoside triacetate 6-*p*-toluenesulphonate, m.p. 170—171°, $[\alpha]_D^{25}$ +7.2° in CHCl_3 , also obtained in 41% yield from β -methyl-*d*-glucoside by $\text{C}_6\text{H}_4\text{Me-SO}_2\text{Cl-C}_5\text{H}_5\text{N}$, followed by Ac_2O , and converted by NaI in COMe_2 into β -methyl-*d*-glucoside triacetate 6-iodide, m.p. 114—115°, $[\alpha]_D^{25}$ +2.4° in CHCl_3 . With Zn dust and a trace of H_2PtCl_6 in 50% AcOH this is reduced to β -methyl-*d*-glucomethyloside triacetate (I), m.p. 103—104°, $[\alpha]_D^{25}$ -12.3° in CHCl_3 . α -Methyl-*d*-glucoside with $\text{C}_6\text{H}_4\text{Me-SO}_2\text{Cl-C}_5\text{H}_5\text{N}$, followed by Ac_2O , affords α -methyl-*d*-glucoside triacetate 6-*p*-toluenesulphonate, a syrup, converted by NaI into the triacetate 6-iodide, m.p. 149—150°, $[\alpha]_D^{25}$ +113.8° in CHCl_3 , and thence into α -methyl-*d*-glucomethyloside triacetate, m.p. 77—78°, $[\alpha]_D^{25}$ +153.6° in CHCl_3 , which with HBr-AcOH yields α -acetobromo-*d*-glucomethyloside, m.p. 150—152° [Micheel, m.p. 135—136° (A., 1930, 455)], $[\alpha]_D^{25}$ +246.6° in CHCl_3 , and thence into (I) by $\text{Ag}_2\text{CO}_3\text{-MeOH}$.

R. S. C.

2-Methyl- and 2:6-dimethyl-galactose. J. W. H. OLDHAM and D. J. BELL (J. Amer. Chem. Soc., 1938, 60, 323—325).—6-Triphenylmethyl- β -methylgalactoside triacetate and 30% fuming HNO_3 give β -methylgalactoside 6-nitrate, m.p. 106—107°, $[\alpha]_D^{17}$

E* (A., II.)

-5° in EtOH, the 3:4-isopropylidene derivative, m.p. 103—104°, $[\alpha]_D$ 0° in CHCl_3 , of which with $\text{MeI-Ag}_2\text{O}$ gives 2-methyl-3:4-isopropylidene- β -methylgalactoside 6-nitrate, m.p. 53—54°. With Na_2S this gives 2-methyl-3:4-isopropylidene- β -methylgalactoside (I), m.p. 75—76°, $[\alpha]_D^{17}$ +7.16° in CHCl_3 , hydrolysed by hot 5% AcOH to 2-methyl- β -methylgalactoside, m.p. 131—132°, $[\alpha]_D^{17}$ +1.69° in H_2O [4:6-benzylidene derivative (II), m.p. 169—170°, $[\alpha]_D^{17}$ -59.4° in CHCl_3], and thence by 5% HCl to 2-methyl- β -galactose, m.p. 147—149°, $[\alpha]_D$ +53° \rightarrow +82.6° in H_2O (gives galactosazone). Methylation ($\text{MeI-Ag}_2\text{O}$) of (I) gives 2:6-dimethyl-3:4-isopropylidene- β -methylgalactoside, m.p. 56—57°, $[\alpha]_D$ -4.46° in CHCl_3 , converted into 2:6-dimethylgalactoside, m.p. 45—46.5°, $[\alpha]_D^{17}$ -23.3° in CHCl_3 (3:4-dinitrate, m.p. 88—88.5°, $[\alpha]_D^{17}$ +3.47°), and 2:6-dimethylgalactose, m.p. 128—130°, $[\alpha]_D$ +46.8° \rightarrow +87.5° in H_2O (gives 6-methylgalactosazone). 4:6-Benzylidene- β -methylgalactoside, m.p. 200°, $[\alpha]_D$ -35.1° in CHCl_3 , or (II) gives 2:3-dimethyl-4:6-benzylidene- β -methylgalactoside, m.p. 148°, $[\alpha]_D$ +18° in CHCl_3 , hydrolysed to 2:3-dimethylgalactose, a syrup, which gives 3-methylgalactosazone.

R. S. C.

Acetals in the sugar group. I. Dimethyl acetal of *d*-galactose. H. A. CAMPBELL and K. P. LINK (J. Biol. Chem., 1938, 122, 635—640).—Penta-acetyl-*d*-galactose Et_2 mercaptal with $\text{HgCl}_2\text{-HgO}$ in MeOH yields the corresponding Me_2 acetal, m.p. 124.5—126°, $[\alpha]_D^{25}$ +20° in MeOH, which is deacetylated by Ba(OH)_2 to *d*-galactose Me_2 acetal, m.p. 120—121°, $[\alpha]_D^{25}$ +16° in H_2O (no mutarotation). When this is hydrolysed by MeOH-HCl , $[\alpha]_D$ first falls to a negative val., and then rises; thus a furanoside is first formed, followed by α -methyl-*d*-galactopyranoside.

E. W. W.

Formation of *l*-tagatose. K. IWADARE and B. KUBOTA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 183—184).—By heating *l*-galactose with $\text{C}_5\text{H}_5\text{N}$, and separating unchanged material by fractional crystallisation, *l*-tagatose, m.p. 133.5—134.5°, $[\alpha]_D^{16}$ +0.6° in H_2O (osazone, m.p. 183.5—184.5°), is obtained.

F. R. S.

α -Fucohexose and α -fucohexitol (methyl-*d*-mannitol). E. VOTOČEK and F. VALENTIN (Chem. Listy, 1938, 32, 33—35).— α -Fucohexonolactone is reduced by Na-Hg to α -fucohexose, $[\alpha]_D$ +17° in H_2O [phenylhydrazone, m.p. 206.5° (decomp.); phenyl-osazone, m.p. 203° (decomp.)], which is further reduced to α -fucohexitol, m.p. 179—180°, $[\alpha]_D$ +0.3° in H_2O .

R. T.

Acidic and fermentative hydrolysis of verbenalloside. Different origins of carbon dioxide formed during two reactions. J. CHEYMOL (J. Pharm. Chim., 1938, [viii], 27, 105—120).—Hydrolysis of 5% aq. verbenalloside by 2.5% H_2SO_4 at 100° is complete in 6—12 hr. [polarimetric determination of the glucose formed, after removal of the verbenol (I)]; 1 mol. of CO_2 is produced anaerobically from the (I), this reaction requiring 18 hr. for completion. Hydrolysis by emulsin at 33° is accompanied by liberation of 1 mol. of CO_2 , which, however, is formed aerobically by oxidation of (I) by an oxidase. Other materials containing β -glucosidases also effect hydrolysis, but at different rates.

R. S. C.

Emulsin. XXXIII. Fermentative fission of mono- and di-glucosides of dihydric phenols. B. HELFERICH and W. REISCHEL (Annalen, 1938, 533, 278—290).—Acetobromoglucose (I) and pyrocatechol- β -D-glucopyranoside tetra-acetate in aq. COMe₂ containing NaOH at room temp. give *pyrocatecholdi- β -D-glucopyranoside octa-acetate*, m.p. 175—177° (corr.), $[\alpha]_D^{25}$ —53.2° in CHCl₃, de-acetylated by NaOMe in MeOH to *pyrocatecholdi- β -D-glucopyranoside* (II), m.p. 220° (decomp.), $[\alpha]_D^{25}$ —86.8° in H₂O. Resorcinoldi- β -D-glucopyranoside octa-acetate, m.p. 210° (corr.), $[\alpha]_D^{25}$ —33.5° in COMe₂, yields *resorcinoldi- β -D-glucoside* (III), $[\alpha]_D^{25}$ —88.3° in H₂O. Quinol is converted by β -glucose penta-acetate (IV) in presence of *p*-C₆H₄Me·SO₃H at 120° into *quinoldi- β -D-glucopyranoside octa-acetate*, m.p. 194° (corr.), $[\alpha]_D^{25}$ —19.5° in CHCl₃, whence *quinoldi- β -D-glucopyranoside* (V), m.p. 262° (corr.), $[\alpha]_D^{25}$ —83.7° in H₂O. Monobenzoylquinol (VI) and (IV) with ZnCl₂ in xylene at 120° give *monobenzoylquinol- α -D-glucopyranoside tetra-acetate*, m.p. 112°, $[\alpha]_D^{25}$ +137.7° in CHCl₃, deacetylated to *quinol- α -D-glucopyranoside* (VII), m.p. 205—206° (corr.), $[\alpha]_D^{25}$ +178.6° in H₂O [corresponding *penta-acetate*, m.p. 100° (corr.), $[\alpha]_D^{25}$ +154° in CHCl₃]. (VI) and (IV) in abs. xylene containing *p*-C₆H₄Me·SO₃H at 115—120° give *monobenzoylquinol- β -D-glucopyranoside tetra-acetate*, m.p. 153—155°, $[\alpha]_D^{25}$ —14.5° in CHCl₃, —16.4° in COMe₂, (VII), (I), and NaOH in aq. COMe₂ at room temp. yield *quinoldi- α -D-glucopyranoside octa-acetate*, m.p. 182° (corr.), $[\alpha]_D^{25}$ +90.9° in CHCl₃, whence *quinoldi- α -D-glucopyranoside* (VIII), m.p. about 245° (decomp.). The β -D-diglucosides are more slowly hydrolysed than the monoglucosides by emulsin of sweet almonds. The differences in the cases of (II), (III), and (V) are 1 : 9, 1 : 3, and 1 : 5, respectively. The diminution in reactivity is ascribed to the partial union of the two sugar residues in the mol. so that addition of the enzyme is less possible than with the monoglucoside. The effect cannot be ascribed to simple substitution of the second OH since methylarbutin is more reactive than arbutin and reactivity is still more pronounced when OH is converted into O·CH₂Ph. Towards yeast α -glucosidase phenol- and quinol- α -D-glucoside and (VIII) act in order of decreasing readiness.

H. W.

Constitution of purine nucleosides. VI. Adenine deoxyriboside, adenine glucoside, and a route to the synthesis of naturally occurring nucleosides. J. M. GULLAND and L. F. STORY (J.C.S., 1938, 259—261).—In their ultra-violet absorption spectra in H₂O, adenine deoxyriboside from thymus and synthetic adenine glucoside resemble 9- and differ from 7-methyladenine. Hence these are 9-substituted adenines.

A. Li.

Trisaccharides from enzymic degradation of starch. III. Constitution of limit dextrins and starch. K. MYRBÄCK (Svensk Kem. Tidskr., 1938, 50, 27—31).—A trisaccharide (mixture) has been obtained from the products of the action of takadiastase on maize starch. It is non-fermentable, contains one reducing group, and gives only a little maltose hepta-acetate when treated with AcCl.

M. H. M. A.

Penetration of water into the lattice of cellulose. Exchange reaction between cellulose and heavy water. G. CHAMPETIER and R. VIALARD (Compt. rend., 1937, 205, 1387—1388; cf. B., 1933, 142).—Exchange occurs between D₂O and cellulose (I) to the extent of three D atoms per glucose group. This indicates that H₂O can penetrate into the interstices of the (I) lattice.

A. J. E. W.

Glyceryl ethers of cellulose. I. P. P. SCHORIGIN and J. A. RIMASCHEVSKAJA (J. Gen. Chem. Russ., 1937, 7, 2428—2436).—Cellulose is treated successively with 33% NaOH and with glyceryl chloride (I) or glycidic alcohol, when ethers containing up to 9 glyceryl groups per C₆H₁₀O₅ unit are obtained. The solubility of the products in H₂O is considerable when pure (I) is used, but falls with increasing concn. of CH(CH₂Cl)₂·OH (II) in the (I) used; (II) alone gives an insol. product.

R. T.

Laboratory experiment involving the Hofmann rearrangement. Preparation of methylaniline hydrochloride from acetamide by means of calcium hypochlorite. C. R. HAUSER and W. B. RENFROW, jun. (J. Chem. Educ., 1937, 14, 542—544).—Directions for the prep. of NH₂Me·HCl (yield 55%) using commercial Ca(OCl)₂ and NaOH instead of Br and alkali are given. Much less NH₄Cl then contaminates the product.

L. S. T.

Colloid chemistry of tetra-alkylammonium salts.—See A., 1938, I, 195.

Co-ordinated zinc compounds with active and racemic propylenediamine.—See A., 1938, I, 207.

New methods of formation of humus. Humic bases. G. BOUILLOUX (Bull. Soc. Chim. biol., 1937, 19, 1654—1662).—Humic bases, well-defined substances analogous to the humic acids, are obtained by heating a mixture of 30 g. of (CH₂)₆N₄ with 25 g. of anhyd. AlCl₃. The residue is dissolved in dil. HCl and the humic base is pptd. as the *picrate*, which is again decomposed. The base is further purified via the ferricyanide; it contains C, H, and N, but no O. On heating to 320—350° it becomes insol. in acids. The solubility in mixtures of CCl₄ and AcOH varies in different preps. The *hydrochloride* can be pptd. by COMe₂. These reactions are consistent with the existence of a "humic radical," very rich in C.

P. G. M.

Complex copper salts of α -amino-acids.—See A., 1938, I, 206.

Syntheses of amino-acid esters of choline. K. FREUDENBERG and R. KELLER (Ber., 1938, 71, [B], 329—334).— α -Azidopropionyl chloride is transformed by NMe₂·CH₂·CH₂·OH in anhyd. Et₂O into β -*dimethylaminoethyl α -azidopropionate*, b.p. 55—56°/0.15 mm., which with MeI gives the corresponding *methiodide*, m.p. 69°, transformed by dry AgCl in COMe₂-MeOH containing a trace of HCl into the *methochloride* (*platinichloride*, decomp. 180°; *aurichloride*, decomp. 132°), hydrogenated (Pd-sponge in H₂O) to *dl-alanylocholine chloride hydrochloride*, HCl·NH₂·CHMe·CO₂·CH₂·CH₂·NMe₂Cl [*platinichloride* (+1H₂O), decomp. 237—239°; *aurichloride*]. The following series of compounds are obtained similarly: β -*dimethylaminoethyl azidoacetate*, b.p. 67°/0.3 mm.,

azidoacetylcholine iodide, m.p. 115°, the *platinichloride*, decomp. 178°, from the corresponding *chloride*, and glycylcholine chloride hydrochloride; *Et* α -azidoisohexanoate, b.p. 90°/11 mm., α -azidoisohexanoic acid, b.p. 87°/0.33 mm., α -azidoisohexoyl chloride, b.p. 72°/11 mm., β -dimethylaminoethyl α -azidoisohexanoate, b.p. 80°/0.35 mm., the corresponding *methiodide*, m.p. 105.5°, and non-cryst. *methochloride* (corresponding *platinichloride*, decomp. 189°, and *aurichloride*, m.p. 102°), and the very hygroscopic *dl*-leucylcholine chloride hydrochloride (*platinichloride*, decomp. 203°; *aurichloride*); α -azidoisovaleryl chloride, b.p. 64°/16 mm., β -dimethylaminoethyl β -azidoisovalerate, b.p. 122°/12 mm., and its *methiodide*, m.p. 111°, and non-cryst. *methochloride* (corresponding *platinichloride*, decomp. 183—184°), the very hygroscopic *dl*-valylcholine chloride hydrochloride (corresponding *platinichloride*, decomp. 205—208°, and *aurichloride*, decomp. 217—218°). *dl*-Alanine and $\text{N}_3\text{CH}_2\text{CO}_2\text{H}$ in alkaline solution yield azidoacetyl-*dl*-alanine, m.p. 101°, from which the corresponding chloride could not be obtained pure. The non-cryst. azidoacetyl-glycine behaves similarly; it is hydrogenated to glycylglycine hydrochloride. H. W.

β' -Diethylaminoethyl β -aminocrotonate. R. L. SHRINER and L. S. KEYSER (J. Amer. Chem. Soc., 1938, 60, 286—288).— $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and PCl_5 in C_6H_6 give a mixture of *cis*- and *trans*- β -chlorocrotonyl chlorides, b.p. 122—140°, converted by $\text{NET}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ in Et_2O into β' -diethylaminoethyl β -chlorocrotonate, b.p. 94—95°/4 mm. (*hydrochloride*, m.p. 114.2—115.2°; *hydrobromide*, m.p. 140—141°), which with liquid NH_3 gives β' -diethylaminoethyl β -aminocrotonate, b.p. 121—122°/3 mm. (*N*-phenylcarbimide derivative, m.p. 87.5°), which has no anæsthetic activity. This may be due to its ready hydrolysis to the keto-ester or to its existence as $\text{NH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$, although n_D^{25} (1.5020) indicates the enamine form. R. S. C.

Equilibrium reaction between *l*(+)-glutamic acid and pyruvic acid, and between *l*(+)-alanine and α -ketoglutaric acid.—See A., 1938, III, 319.

Synthesis of α -amino- β -hydroxy-*n*-butyric acids. V. Preparation of *dl*-allothreonine; addition of methyl hypobromite to unsaturated acids. H. D. WEST, G. S. KRUMMEL, and H. E. CARTER. VI. Preparation of *d*- and *l*-allothreonine, and nutritive value of the four isomerides. H. D. WEST and H. E. CARTER (J. Biol. Chem., 1938, 122, 605—609, 611—617; cf. A., 1937, II, 328).—V. The general reaction $\text{CHR}\cdot\text{CH}\cdot\text{CO}_2\text{H} + \text{MeOBr} \rightarrow \text{OMe}\cdot\text{CHR}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ is effected by mixing the unsaturated acid with Br, both in MeOH, in presence of AgNO_3 (when formation of the Br_2 -acid is hindered), removing AgBr and excess of Br, making alkaline, concentrating and extracting with Et_2O , and pptg. the Br-acid by H_2SO_4 . In this way, crotonic acid gives α -bromo- β -methoxy-*n*-butyric acid (I), m.p. 62—63°, b.p. 126—130°/8 mm., which is convertible, not into *dl*-threonine, but into *dl*-allothreonine (cf. *loc. cit.*). Cinnamic acid (II) yields the α -bromo- β -methoxy- β -phenylpropionic acid of m.p. 183—184° only; *allo*-cinnamic acid also gives this [probably via (II)], but mainly the acid of m.p. 139—140°. Since the product from crotonic acid and ICl (A., 1928, 1131)

can give rise to *dl*-allothreonine, it is an α -iodo- β -methoxybutyric acid of the same optical configuration as (I).

VI. From *dl*-allothreonine (above), the *formyl*-*dl*-*O*-methyl derivative (A., 1937, II, 328) is converted into *brucine formyl*-*l*(-)-, m.p. 132—136°, $[\alpha]_D^{25} -22.5^\circ$, and *d*(-)-*O*-methylallothreonine, m.p. 186—188°, $[\alpha]_D^{25} -19.9^\circ$, and these are hydrolysed to *l*(-)-, m.p. 269—272°, $[\alpha]_D^{25} -9.11^\circ$ (*N*-Bz derivative, m.p. 127—128°, $[\alpha]_D^{25} -17.0^\circ$), and *d*(+)-allothreonine, m.p. 268—272°, $[\alpha]_D^{25} +9.60^\circ$ (*N*-Bz derivative, m.p. 128—129°, $[\alpha]_D^{25} +17.1^\circ$). Of the two *allothreonines*, and *l*(+)- and *d*(-)-threonine, only the last one will support the growth of rats on an otherwise adequate diet. E. W. W.

Metabolism of *N*-benzenesulphonyl-*N*-methyl derivatives of α -aminoadipic, *l*-aspartic, and *d*-glutamic acid. B. FLASCHENTRÄGER, K. BERNHARD, P. FABER, H. WALDMANN, and C. WOLFENBERGER (Z. physiol. Chem., 1937, 250, 189—191).—Methylation of *N*-benzenesulphonylaspartic acid yields *N*-benzenesulphonyl-*N*-methyl-*l*-aspartic acid, m.p. 171—173°, $[\alpha] -54^\circ$ in EtOH , -45° in $2\text{N}\cdot\text{AcOH}$, -42° in H_2O . *N*-Benzenesulphonyl-*N*-methyl-*d*-glutamic acid, m.p. 138—139°, $[\alpha]_D^{25} -28.8^\circ$ in EtOH , is similarly prepared from benzenesulphonylglutamic acid, m.p. 129—132°, $[\alpha]_D^{25} -1.12^\circ$ in H_2O (*Na* salt). Subcutaneous injection of the acids into dogs is followed by excretion of approx. 70—80% of the unchanged acid in the urine. F. O. H.

Diamino-acid, canavanine. VI. Deaminated canavanine. M. KITAGAWA and J. TSUKAMOTO (J. Biochem. Japan, 1937, 26, 373—385; cf. A., 1937, II, 402).—Canavanine is stable when heated in acid solution but when heated in the free state in H_2O forms deaminocanavanine, $\text{NH}\langle\begin{smallmatrix} \text{O}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{C}(\text{NH})\cdot\text{NH} \end{smallmatrix}\rangle\text{CH}\cdot\text{CO}_2\text{H}$, m.p. 256—257° (decomp.), $[\alpha]_D^{25} +26.61^\circ$ in H_2O , $[\alpha]_D^{25} -45.14^\circ$ in (equiv. amount of) aq. NaOH (*Bz*₂ derivative, m.p. 150—163°; *Et* ester *hydrochloride*, m.p. 135°); small amounts of another NH_2 -acid, which also occurs in jack-bean meal, are produced. F. O. H.

Diacetoneamine, diacetonealkamine, and 2 : 4 : 4 : 6-tetramethyl-4 : 5-dihydro-1 : 3-oxazine. (Miss) M. E. SMITH and H. ADKINS (J. Amer. Chem. Soc., 1938, 60, 407—409).—Diacetoneamine, readily obtained from $\text{CMe}_2\cdot\text{CH}\cdot\text{COMe}$ and liquid NH_3 , gives the *Ac* derivative, m.p. 46—46.5°, b.p. 93—97°/1 mm., reduced by H_2 -Raney Ni at 160—170°/100—200 atm. in dioxan to δ -acetamido- δ -methyl-*n*-pentan- β -ol (I), m.p. 87.5—89°, which at 140—160° loses H_2O to yield 2 : 4 : 4 : 6-tetramethyl-4 : 5-dihydro-1 : 3-oxazine, b.p. 146.8—147°/737 mm., 50—51°/17 mm. (*picrate*, m.p. 152—153°). This is unaffected by MgMeI or *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, is reduced (Raney Ni) to $\text{NHEt}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, reverts to (I) in the presence of H_2O , and is converted by hot 10% NaOH into NaOAc and $\text{NH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, b.p. 74.5—75.5°/15 mm. Attempts to reduce the keto- and OH-amines failed and attempts to dehydrate the latter were without effect or eliminated NH_3 . R. S. C.

Hydrazides of higher unsaturated acids. A. OSKERKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1937, 4, 329—340).—A *hydrazide*, m.p. 75—75.5°, of stearic acid was prepared. Its EtOH solution reduces $\text{NH}_3\text{-AgNO}_3$ or Fehling's solution on warming, and forms the *compound*, $\text{C}_{17}\text{H}_{31}\text{-CO-NH-NH}_2\text{-HCl}$ with HCl. It condenses with COMe_2 and PhCHO , and gives with Ac_2O a *cryst. Ac derivative*, m.p. 111—112°. On warming with I the *compound*, $(\text{C}_{17}\text{H}_{31}\text{-CO-NH})_2$, m.p. 122—123°, is formed.

H. J. E.

Synthesis of azido-derivatives of acetylene hydrocarbons. S. FRIEDMANN (Mem. Inst. Chem. Ukrain. Acad. Sci., 1937, 4, 341—350).—The action of CPh:CNa with β -azidoethyl chloride gives an unstable product which evolves N_2 . This gives with Br a *cryst. substance*, m.p. 156—157°.

H. J. E.

Oxidation of azido-compounds. S. FRIEDMANN (Mem. Inst. Chem. Ukrain. Acad. Sci., 1937, 4, 351—357).—The N_3 group of γ -azido- α -chloropropane, allyl azide (I), and azidoethyl alcohol (II) resists oxidation with KMnO_4 . (II) gives $\text{N}_3\text{-CH}_2\text{-CO}_2\text{H}$ (III). (I) gives (III) and HCO_2H .

H. J. E.

Structure of the diammoniate of diborane. [Preparation of Me_2OBH_3 .]—See A., 1938, I, 207.

Association of organoboric acids. H. E. FRENCH and S. D. FINE (J. Amer. Chem. Soc., 1938, 60, 352—353).— BPh(OH)_2 , $\text{BBu}^t(\text{OH})_2$, and $n\text{-C}_5\text{H}_{11}\text{-B(OH)}_2$ are shown cryoscopically to be associated in C_6H_6 , but not in PhNO_2 or dioxan. Bu^t_3BO_3 is not associated, even in C_6H_6 .

R. S. C.

Synthesis of triethylvinylsilane. S. N. USCHAKOV and A. M. ITENBERG (J. Gen. Chem. Russ., 1937, 7, 2495—2498).— SiEt_4 and Cl_2 in presence of PCl_5 yield a mixture of triethyl- α -, b.p. 80—82°/9 mm., and β -chloroethylsilane, b.p. 72—73°/9 mm.; the former reacts with $n\text{-NaOH}$ in EtOH at 145°, but not at the b.p., to yield triethylvinylsilane, b.p. 146°, into which the latter is converted quantitatively at the b.p.

R. T.

Mercuric halides of dimethyl telluride. F. CARR and T. G. PEARSON (J.C.S., 1938, 282).— TeMe_2 and Hg halides in COMe_2 yield *Me₂ telluride Hg^{II} chloride*, m.p. 179° (decomp.), *bromide*, m.p. 160—161° (decomp.), and *iodide*, m.p. 107° (slight decomp.).

A. Li.

Modified Grignard reaction in the synthesis of hydrocarbons. J. W. H. OLDHAM and A. R. UBBELOHDE (J.C.S., 1938, 201—206).—Alkyl or benzyl halides (RX) with Mg in Et_2O yield by three concurrent reactions MgRX , R_2 , and $\text{RH} +$ (unsaturated) R'H . Chlorides give chiefly MgRCl , but alkyl iodides yield up to 25%, and CH_2PhI 38%, of R_2 . Repeated alternate additions of I (to decompose MgRI) and Mg to the reaction mixture increase the yield of R_2 to 65% ($\text{R} = \text{C}_{12}\text{H}_{25}$, $\text{C}_{16}\text{H}_{33}$, or CH_2Ph). $\text{C}_{12}\text{H}_{25}\text{-MgI}$ when boiled for 6½ hr. with $\text{C}_{12}\text{H}_{25}\text{I}$ gives 40% of $\text{C}_{12}\text{H}_{26}$ and $\text{C}_{12}\text{H}_{24}$.

A. Li.

Alkoxides of internally complex compounds of tervalent iron. B. EMMERT and W. SEEBODE (Ber., 1938, 71, [B], 242—245; cf. A., 1934, 379).—Passage of O_2 through Fe^{II} diacetylacetone ($+2\text{C}_5\text{H}_5\text{N}$) in $\text{CH}_2\text{Ph-OH}$ at 35° gives the *compound*,

$(\text{C}_5\text{H}_7\text{O}_2)_2\text{-Fe-O-CH}_2\text{Ph}$, m.p. about 124°. Similarly $\text{CO}(\text{CH}_2\text{Bz})_2$ affords the *substance*, $\text{C}_{27}\text{H}_{25}\text{O}_5\text{Fe}$, m.p. 174° (decomp.). CH_2Bz_2 yields *substances* $(\text{C}_{15}\text{H}_{11}\text{O}_2)_2\text{-Fe-OR}$ in which $\text{R} = \text{Me}$, m.p. 256°, $= \text{Et}$, m.p. 246°, $= \text{CH}_2\text{Ph}$, all of which are transformed by excess of NHPh-NH_2 into the Fe^{II} *compound* $(\text{C}_{15}\text{H}_{11}\text{O}_2)_2\text{-Fe(NHPh-NH}_2)_2$. Analogously $(\text{C}_5\text{H}_7\text{O}_2)_2\text{-Fe-OEt}$ gives the *compound*, $(\text{C}_5\text{H}_7\text{O}_2)_2\text{-Fe(NHPh-NH}_2)_2$ although Fe^{II} in complex union with a diketone residue is not attacked by excess of NHPh-NH_2 . The *substance*, $(\text{C}_{15}\text{H}_{11}\text{O}_2)_2\text{-Fe(OPh)}_2$, m.p. about 274° after becoming black at 250°, is described. $\text{CH}_2\text{Ac-CO}_2\text{Et}$ gives the *compound*, $(\text{C}_6\text{H}_5\text{O}_3)_2\text{-Fe(OMe)}_2$, m.p. 135° (decomp.), whilst $o\text{-OH-C}_6\text{H}_4\text{-CHO}$ affords the *substances*, $\text{C}_9\text{H}_{11}\text{O}_4\text{Fe}$, m.p. 185°, and $\text{C}_{16}\text{H}_{15}\text{O}_5\text{Fe}$, m.p. 174° (decomp.), in MeOH and EtOH, respectively.

H. W.

Absorption and optical activity of double-nuclear cobalt compounds.—See A., 1938, I, 122.

Organic reaction of boron fluoride. XIX. Condensation of cyclopropane and olefines with acids. T. B. DAVIS and F. J. SOWA (J. Amer. Chem. Soc., 1938, 60, 358—359; cf. A., 1938, II, 88).— BF_3 and cyclopropane convert AcOH , $\text{CHCl}_3\text{-CO}_2\text{H}$, and BzOH into the Pr^a esters. C_3H_6 and BF_3 , best in $\text{C}_2\text{H}_2\text{Cl}_4$, produce the Pr^a esters of *p*-nitro-, *o*-chloro-, *o*- and *p*-amino-benzoic and furoic acid and $\text{CH}_2\text{Ph-CO}_2\text{H}$ in fair to poor yield with much polymerised material. C_4H_8 gives Bu^tOAc (32%) and Bu^sOAc (8%); an amylene mixture gave a worse yield of mixed esters. cycloPropane and H_2SO_4 at -3° give 95% of Pr^aSO_4 .

R. S. C.

[Catalytic] promotion in the conversion of cyclohexane into benzene or methane.—See A., 1938, I, 205.

General chemical method for the preparation of deuterated benzenes. A. LANGSETH and A. KLIT (Danske Vidensk. Selskab., 1937, 15, No. 13, 3—22).—Deuterobenzenes are prepared (60—80% yield) by passing DCl (from SOCl_2 and D_2O) into a mixture of the corresponding halogen compound, Et_2O , and Mg, regulating the flow of DCl so that C_6H_6 is not continuously evolved. In this way PhBr , 1 : 2- and 1 : 3- $\text{C}_6\text{H}_4\text{BrI}$, 1 : 4- $\text{C}_6\text{H}_4\text{Br}_2$, 1 : 5 : 6- and 1 : 4 : 6- $\text{C}_6\text{H}_3\text{Br}_2\text{I}$, 1 : 3 : 5- $\text{C}_6\text{H}_3\text{Br}_3$, 1 : 2 : 5 : 6-, 1 : 3 : 5 : 6-, and 1 : 3 : 4 : 6- $\text{C}_6\text{H}_2\text{Br}_3\text{I}$, and 1 : 2 : 3 : 5 : 6- $\text{C}_6\text{HBr}_4\text{I}$ yield the corresponding deuterated benzenes.

A. Li.

Isomerisation accompanying alkylation: alkylation of benzene with isopropylethylene in the presence of sulphuric acid. V. N. IPATEV, H. PINES, and L. SCHMERLING (J. Amer. Chem. Soc., 1938, 60, 353—354).— $\text{CH}_2\text{-CHPr}^i$ is isomerised by H_2SO_4 at 0° during alkylation of C_6H_6 , as it yields *tert*-.amylbenzene, b.p. 188—189° [NHAc , m.p. 141—142°, and (NHAc)₂-derivative, m.p. 180—181°], also obtained from $\text{CMe}_2\text{-CHMe-CHMe-CHEt}$ mixtures and synthesised as follows. *p*-*tert*-.Amylphenol gives ($\text{H}_2\text{-Ni}$) 4-*tert*-.amylcyclohexanol, dehydrated by Al_2O_3 at 427° to *tert*-.amylcyclohexene, b.p. 193—197°, which is hydrogenated (Ni) in $n\text{-C}_5\text{H}_{12}$ at 150°/100 atm. to *tert*-.amylcyclohexane, dehydrogenated by $\text{Pt-Al}_2\text{O}_3$ at 250°. CPhMe-CMe_2 and $\text{H}_2\text{-Ni}$ in isopentane at

50°/100 atm. give β -methyl- γ -phenyl-n-butane, b.p. 184° [NHAc, m.p. 147—148°, and (NHAc)₂-derivative, m.p. 193°]. R. S. C.

Action of elementary fluorine on organic compounds. V. N. FUKUHARA and L. A. BIGELOW (J. Amer. Chem. Soc., 1938, 60, 427—429; cf. A., 1937, II, 479).—C₆Cl₆ vapour and F₂ in the presence of Cu gauze at 55° give a reactive liquid, converted by Fe-AcOH into twelve substances, having Cl:F ratios as stated in parentheses, b.p. 32°/11 mm., a glass (2:4.94), b.p. 37°/11 mm., m.p. -41° (4:8.96), b.p. 41°/11 mm., a glass (1:2), b.p. 45°/11 mm., m.p. -56° (2:3.02), b.p. 52°/11 mm., a glass (3:5.01), b.p. 56°/11 mm., a glass (3:5.01), b.p. 64°/11 mm., m.p. -44° (2:3.02), b.p. 68°/11 mm., m.p. -5° (4:5.04), b.p. 72°/11 mm., m.p. 0° (5:6.05), b.p. 75°/11 mm., m.p. -9° (2:1), m.p. 69—70° (5:2.98), and m.p. 142—143° (4:1.01). R. S. C.

Preparation of benzotrifluoride. J. H. SIMONS and C. J. LEWIS (J. Amer. Chem. Soc., 1938, 60, 492).—75—95% yields are obtained from CPhCl₃ and gaseous HF in a Cu vessel. R. S. C.

Strecker's reaction. N. TURKIEWICZ and S. PILAT (Ber., 1938, 71, [B], 284—285).—The following Na-sulphonates are obtained by heating the requisite ohloride with Na₂SO₃·7H₂O in a rotating autoclave at 200° (the bromides are more readily hydrolysed to the corresponding alcohols): benzyl-, m.p. >310°; 2-naphthylmethyl-, cetyl-, cyclopentyl-. Hg cyclopentyl chloride has m.p. 108.5°. H. W.

Mesomeric effect of the sulphoxide group. D. L. HAMMICK and R. B. WILLIAMS (J.C.S., 1938, 211—215).—The electric dipole moment of Bu₂SO in C₆H₆ is 3.90 D., i.e., < that of Ph₂SO, 4.08 D. Hence SO has a negative mesomeric effect, confirmed by the fact that *m*-iododiphenyl sulphoxide, m.p. 73.5° (from *m*-NO₂-C₆H₄-SPh → *m*-NH₂-C₆H₄-SPh → *m*-C₆H₄I-SPh, oxidised by H₂O₂ in AcOH), is not hydrolysed by EtOH-KOH, whilst the *p*-isomeride is. A. Li.

Kinetics of catalysed polymerisation of styrene. See A., 1938, I, 204.

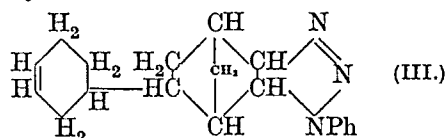
Diphenyl and its derivatives. XVI. Passage from the diphenyl to the fluorene system: synthesis of 2-methylfluorene. L. MASCARELLI and B. LONGO (Gazzetta, 1937, 67, 812—816; cf. A., 1937, II, 185).—*o*-C₆H₄MeI and 1:4:3-C₆H₃MeI-NO₂ give (Cu) 2'-nitro-2:4'-dimethyldiphenyl, m.p. 140°, reduced (SnCl₂) to the 2'-NH₂-compound [hydrochloride (+H₂O), m.p. 213—214° (decomp.)], which with HNO₂ gives 2-methylfluorene. *o*-C₆H₄MeCl and 1:4:3-C₆H₃MeCl-NO₂ give only 2:2'-dinitro-4:4'-dimethyldiphenyl; *sym.* products are also obtained from other compounds. E. W. W.

Brominations with iodine monobromide. W. MILTZER (J. Amer. Chem. Soc., 1938, 60, 256—257).—IBr acts as a brominating agent in AcOH at 50°, 4:1-C₁₀H₆Br-OH and 1-C₁₀H₇Br being conveniently prepared in this way. R. S. C.

Structure and reactivity of the naphthalene nucleus. II. Oxidation-reduction reactions and substitution in naphthalene derivatives. V. N.

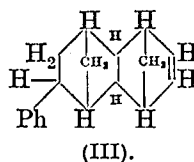
UFIMTZEY (J. Gen. Chem. Russ., 1937, 7, 2402—2405).—Polemical, against Joffe (A., 1937, II, 373). R. T.

Polymerisation of hydrocarbons. VIII. Trimeride of butadiene. K. ALDER and H. F. RICKERT (Ber., 1938, 71, [B], 373—378).— Δ^3 -Vinylcyclohexeno (I) and butadiene (II) in presence of a little (C-CO₂H)₂ [to repress the chain polymerisation of (II)] give Δ^3 :3'-octahydrodiphenyl, b.p. 230—232°, hydrogenated (PtO₂ in EtOAc) to dodecahydrodiphenyl, b.p. 234°, and dehydrogenated by Br at 200° to 4:4'-dibromodiphenyl, m.p. 163°. cyclopentadiene and (I) at 180—190° give a small yield of 2:5-endomethylene- Δ^3 :3'-octahydrodiphenyl, b.p. 110—118°/11 mm., characterised as the hydrotriazole (III), m.p. 155°.

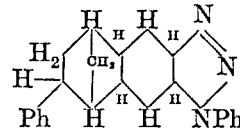


H. W.

Diene syntheses. IV. Formation of diphenyl and fluorene ring systems; arylated ethylenes as olefinic components for diene syntheses. K. ALDER and H. F. RICKERT (Ber., 1938, 71, [B], 379—386).—If the tendency towards chain polymerisation is repressed by the presence of (C-CO₂H)₂, butadiene and CHPh:CH₂ at 170—180° afford 1:2:5:6-tetrahydrodiphenyl, b.p. 98—115°/11 mm., identified by hydrogenation (Pd in EtOAc) to cyclohexylbenzene and by dehydrogenation (Se at 350—360°) to Ph₂. Similarly, β - γ -dimethylbutadiene (I) and CHPh:CH₂ at 180° give 3:4-dimethyl-1:2:5:6-tetrahydrodiphenyl, b.p. 128—130°/11 mm. CHPh:CH₂ and cyclopentadiene (II) at 180—190° yield 2:5-endomethylene-1:2:5:6-tetrahydrodiphenyl, b.p. 122—124°/vac. (hydrogenated to 2:5-endomethylene-1:2:3:4:5:6-hexahydrodiphenyl, b.p. 123—125°/11 mm., and transformed by PhN₃ into the hydrotriazole, C₁₉H₁₉N₃, m.p. 134—135°), and the hydrocarbon (III), b.p. 163—165°/vac., which adds 2H giving a compound, b.p. 185—190°/11 mm., and gives the



(III.)



(IV.)

hydrotriazole (IV), m.p. 217—218°. Indene (V) with butadiene gives Δ^2 -tetrahydrofluorene, b.p. 116—118°/11 mm., dehydrogenated (Se at 350°) to fluorene and with (I) yields 2:3-dimethyl-tetrahydrofluorene, b.p. 146—148°/11 mm., dehydrogenated (Se at 350°) to 2:3-dimethylfluorene, m.p. 125—126°. (II) and (V) at 180—190° yield 1:4-endomethylenetetrahydrofluorene, b.p. 135—136°/vac., converted into the hydrotriazole, C₂₀H₁₉N₃, m.p. 189°, and the hydrocarbon (VI), m.p. 105° (corresponding hydrotriazole, C₂₅H₂₅N₃, m.p. 225°). H. W.

Synthesis of 1:4-dimethylphenanthrene by cyclodehydration methods. D. PAPA, D. PERL-

MAN, and M. T. BOGERT (J. Amer. Chem. Soc., 1938, 60, 319—321).— β -*p*-Xylylethyl alcohol [prep. from 1:4:2- $C_6H_3Me_2Br$ and $(CH_2)_2O$ in 61% yield], b.p. 108—111°/4 mm. (*phenylurethane*, m.p. 79—79.5°), and HBr give the bromide, b.p. 107—111°/6 mm., the Mg derivative of which with *cyclohexanone* yields 1- β -*p*-xylylethylcyclohexanol, b.p. 160—162°/3 mm. (*phenylurethane*, m.p. 85—86°), dehydrated by P_2O_5 in 82% yield to 1:4-dimethyl-5:6:7:8:9:10:13:14-octahydrophenanthrene (I), b.p. 154—156°/6 mm., and a small amount of (?) spiran. 2-Methylcyclohexanone affords similarly 2-methyl-1- β -*p*-xylylethylcyclohexanol, b.p. 159—161°/2 mm. (*phenylurethane*, m.p. 144—145°), and 1:4:13-trimethyl-5:6:7:8:9:10:13:14-octahydrophenanthrene (II), b.p. 155—156°/4 mm. Se at 340—350° converts (I) or (II) into 1:4-dimethylphenanthrene, m.p. 49.5—50° (picrate, dimorphic, m.p. 140° and 143.5°), without apparent migration of Me. M.p. are corr. R. S. C.

Synthesis of 3:4-benzphenanthrene. M. S. NEWMAN and L. M. JOSHEL (J. Amer. Chem. Soc., 1938, 60, 485—488).— $CHPh_2 \cdot CHO$ and $CN \cdot CH_2 \cdot CO_2Et$ with a little NH_4Et_3 and $AcOH$ give 12—21% of β -benzhydrylgutaric acid, m.p. 177.6—178.2° (anhydride, m.p. 177—177.4°), the dichloride of which with $AlCl_3$ in $C_2H_5Cl_4$ gives a 51.7% yield of 2:9-diketo-1:2:9:10:11:12-hexahydro-3:4-benzphenanthrene, m.p. 234—234.4° (sinters at 231.6°). This gives a *disemicarbazone*, decomp. 266—268°, reduced ($NaOEt$) to a hydrocarbon, which with S yields 3:4-benzphenanthrene. The diketone and $MgMeI$ or $MgEtI$ affords an $(OH)_2$ -compound, which after dehydration by I and dehydrogenation by S at 220—240° gives 47.4% of 2:9-dimethyl-, m.p. 130.6—131° (picrate, m.p. 164.6—165°), and 42% of 2:9-diethyl-3:4-benzphenanthrene, m.p. 106.4—107° [s - $C_6H_3(NO_2)_3$ additive compound, m.p. 182.4—183.2°], respectively. M.p. are corr. 6:7-Dimethyl-3:4-benzphenanthrene is not carcinogenic. R. S. C.

Polycyclic aromatic hydrocarbons. XVI. 1:2:3:4-dibenzphenanthrene. C. L. HEWERT (J.C.S., 1938, 193—196).—*cyclohexanone* with Mg β -9-phenanthrylethyl chloride (Bergmann *et al.*, A., 1936, 1371) gives 1-(β -9'-phenanthrylethyl)- Δ^1 -cyclohexene, b.p. 205—206°/0.4 mm. (picrate, m.p. 120—121°), cyclised by $AlCl_3$ in CS_2 to dihydrobenzanthrene-spirocyclohexane (?), m.p. 131—132°, unaffected by heating with Se. Et potassiocyclohexane-2-carboxylate with β -9-phenanthrylethyl bromide, m.p. 86—86.5° (from the alcohol and PBr_3 in CCl_4), yields Et 2-(β -9'-phenanthrylethyl)cyclohexanone-2-carboxylate [hydrolysed to α -(β -9-phenanthrylethyl)pimelic acid, m.p. 86—90°], which could not be cyclised with dil. H_2SO_4 . 1:2:3:4-Dibenzphenanthrene (I), m.p. 114.5—115° (picrate, m.p. 140—140.5°), was prepared by heating Na 9-phenanthrylacetae with o - $NO_2 \cdot C_6H_4 \cdot CHO$ and Ac_2O , giving o -nitro- α -(9-phenanthryl)cinnamic acid, m.p. 214—215°, reduced by $Fe(OH)_2$ to the NH_2 -acid, m.p. 195—196°. When diazotised and heated at 50° with Cu this yields 1:2:3:4-dibenz-10-phenanthroic acid, m.p. 267—268° [together with 3-(9'-phenanthryl)coumarin], converted into (I) by boiling with Cu-bronze in quinoline. (I) is oxidised ($Na_2Cr_2O_7$ - $AcOH$) to the quinone, m.p.

237—238°, and with o - $C_6H_4(NH_2)_2$ gives an *azine*, m.p. 242—243°. A. LI.

[Coronene.] R. SCHOLL and K. MEYER (Ber., 1938, 71, [B], 407; cf. A., 1938, II, 20).—The production of coronene by the destructive hydrogenation of coal promises a material reasonable in price.

H. W.

Physiologically active phenylethylamines. I. Hydroxy- and methoxy- β -phenyl- α -methylethylamines. E. H. WOODRUFF and T. W. CONGER (J. Amer. Chem. Soc., 1938, 60, 465—467).—The appropriate aldehyde and ketone give $COMe \cdot CMe \cdot CHPh$, o -, b.p. 162—163°/12 mm., m -, b.p. 120—122°/0.05 mm., and p -methoxy- α -methylstyryl Me ketone, b.p. 173—174°/12 mm., oxidised by $HOHal$ to the α -methylcinnamic acids (p -OMe-acid, new m.p. 155—157°), which are converted into β -phenylisobutyric acid, b.p. 146—149°/6 mm., β - o -, m.p. 62—63°, b.p. 132—136°/0.04 mm. (amide, m.p. 114—115°), m -, b.p. 142—144°/0.02 mm. (amide, m.p. 106—107°), and p -anisylisobutyric acid, b.p. 132—134°/0.005 mm., 308°/760 mm., m.p. 40° (amide, m.p. 126.5°), β -phenyl-, b.p. 102—104°/22 mm. (hydrochloride, m.p. 152°), β - o -, b.p. 118—120°/11 mm. (hydrochloride, m.p. 101—103°), and m -anisylisopropylamine, b.p. 124—126°/11 mm. (hydrochloride, m.p. 112—113°), and β - o -, m.p. 159°, and m -hydroxyphenylisopropylamine hydrochloride, m.p. 138°.

R. S. C.

Reactions of $\alpha\beta$ -unsaturated cyclic aldehydes and ketones. I. Their conversion into anilines. R. G. COOKE and A. K. MACBETH (J.C.S., 1937, 1593—1596).—4-*iso*Propyl- Δ^2 -cyclohexenoneoxime when refluxed (4 hr.) with Ac_2O - $NaOAc$ gives 4-isopropylacetanilide (cf. A., 1937, II, 345), hydrolysed by 70% H_2SO_4 to cumidine (I). Similarly, piperitoneoxime yields thymylamine (3:6- $C_6H_3MePr^s \cdot NH_2$) (II) (oxalate, m.p. 169°), and carboxime yields carvacrylamine (2:5- $C_6H_3MePr^s \cdot NH_2$) (oxalate, m.p. 150°). The absorption spectra of (I), (II), their Ac derivatives, and p - $C_6H_4Me \cdot NH_2$ in EtOH and in 10% HCl are recorded. H. G. M.

Syntheses with acetoacetdiphenylamide. B. M. DUBININ and G. V. TSHELINCEV (J. Gen. Chem. Russ., 1937, 7, 2365—2372).— $CH_2 \cdot Ac \cdot CO \cdot NPh_2$ (I) in conc. H_2SO_4 at room temp. yields 2-keto-1-phenyl-4-methyl-1:2-dihydroquinoline (II), m.p. 134—135°. (I) and MeI or EtI in $NaOEt$ -EtOH give α -methyl- (III), m.p. 83°, or α -ethyl-acetoacetdiphenylamide, m.p. 70—71°, from which 2-keto-1-phenyl-3:4-dimethyl-, m.p. 156—157°, or -4-methyl-3-ethyl-1:2-dihydroquinoline, m.p. 116—117°, is obtained as above. (III) and $NaOEt$ -EtOH react with MeI to yield isobutyrodiphenylamide, m.p. 63—64°, not yielding a quinoline derivative when treated with H_2SO_4 . A cryst. product was not obtained from α -benzylacetoacetdiphenylamide, m.p. 108—109° [from (I), CH_3PhI , and $NaOEt$]. (I) in Et_2O , Na, and $AcCl$ yield α -diacetoacetdiphenylamide, m.p. 123—124°, which with H_2SO_4 yields (II). R. T.

Bromination of nitrodiphenyls. F. H. CASE (J. Amer. Chem. Soc., 1938, 60, 424—427).— p - $C_6H_4Ph \cdot NO_2$ (I), Br, and $FeCl_3$ in $AcOH$ or H_2O give 4- and 2-bromo-4'-nitrodiphenyl (II). The

compound, m.p. 102°, of Guglielmelli *et al.* (A., 1932, 1240) was thus probably a mol. compound of (I) and (II) and the derived compounds were mixtures. The Ac derivative of 4-nitro-4'-aminodiphenyl (modified prep.), Br, and NaOAc in AcOH give 3-bromo-4'-nitro-4'-acetamidodiphenyl, m.p. 236—237°, hydrolysed to 3-bromo-4'-nitro-4'-aminodiphenyl, m.p. 118—119°, which affords (HNO₂-EtOH) 3-bromo-4'-nitrodiphenyl, m.p. 94—95°, also prepared from *m*-C₆H₄Br·N₂·ONa and PhNO₂, and reduced by SnCl₂ to 3-bromo-4'-aminodiphenyl, m.p. 64—65° (Ac derivative, m.p. 182—183°; with CrO₃ gives *p*-C₆H₄Br·CO₂H). 3:4'-Dibromo-4-aminodiphenyl and HNO₂-EtOH give 3:4'-dibromodiphenyl, b.p. 175—177°/3 mm., oxidised to *p*-C₆H₄Br·CO₂H. SnCl₂ reduces (II) to 2-bromo-4'-aminodiphenyl, b.p. 183—185°/3 mm. (Ac derivative, m.p. 155—156°), converted (Gattermann) into 2:4'-dibromodiphenyl, m.p. 55—56°. *o*-C₆H₄BrI, *m*-C₆H₄I·NO₂, and Cu at 250° afford 2-bromo-3'-nitrodiphenyl, m.p. 78—79° (and a little 3:3'-dinitrodiphenyl), reduced to 2-bromo-3'-aminodiphenyl, m.p. 57° (Ac derivative, m.p. 135°). Br-AcOH converts *m*-C₆H₄Ph·NO₂ into much 4- and a little 2-bromo-3'-nitrodiphenyl. *o*-C₆H₄Ph·NO₂ yields much 4- and a little 2-bromo-2'-nitrodiphenyl. R. S. C.

Structure of the "nitrenes." T. W. J. TAYLOR, J. S. OWEN, and D. WHITTAKER (J.C.S., 1938, 206—209; cf. Staudinger and Miescher, A., 1919, i, 584).—Addition of CPh₂·CO to *N*-methylbenzophenone-oxime yields 2-keto-3:3:4:4-tetraphenyl-1-methyl-trimethyleneimine oxide, m.p. 164°, and to *N*-phenylbenzaloxime, 2-keto-1:3:3:4-tetraphenyltrimethyleneimine oxide, m.p. 199—200° (lit. 186—190°), which when heated yields the "triphenyl-*N*-phenylnitrene" of Staudinger and Miescher (*loc. cit.*), for which the structure 1:2:2:3-tetraphenylethyleneimine (I) is suggested. Reduction (Al-Hg, moist Et₂O) of (I) yields *α*-anilino-*αα*-triphenylethane, m.p. 152—153° (NO-derivative, m.p. 114—115°). MgPhBr and CPh·CHPh·NHPh in Et₂O yield *β*-anilino-*αα*-triphenylethyl alcohol, m.p. 173°, which with PCl₅ in (·CH₂Br)₂ yields *α*-chloro-*β*-anilino-*αα*-triphenylethane (II), m.p. 196°, which could not be converted into (I). Similarly NHPh·CHPh·CHPh·OH with PCl₅ in CHCl₃ yields *α*-chloro-*β*-anilino-*αβ*-diphenylethane, m.p. 122°, which with KOH-EtOH yields 1:2:3-triphenylethyleneimine, m.p. 99°.

J. D. R.

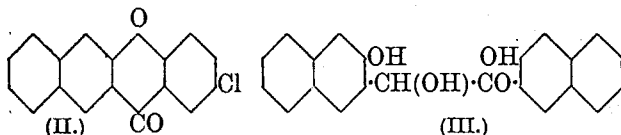
Symmetrical [di]-sec.-diamines derived from *αα*-diaminoethane. J. T. L. B. RAMEAU (Rec. trav. chim., 1938, 57, 194—214; cf. van Alphen, A., 1935, 337; Lob, A., 1936, 1501).—The Schiff's bases obtained from (·CH₂·NH₂)₂ and *p*-OMe·C₆H₄·CHO, Pr^oCHO, and furfuraldehyde (I) are reduced (Na, EtOH) to *NN'*-disubstituted ethylenediamines, which react readily with AlkCHO and ArCHO to give 1:2:3-trisubstituted tetrahydroglyoxalines (readily hydrolysed by dil. acids to the original components). A Schiff's base was not obtained from CH₂Ph·CHO (resin formation), but reduction of the condensation product gives small amounts of (III) (below) and *α*-amino-*β*-(*β'*-phenylethylamino)ethane, b.p. 120—125°/12 mm. [NN'-Bz₂, m.p. 124°, -di-

(phenylcarbonyl), m.p. 169—170°, and -di-(*α*-naphthylcarbonyl), m.p. about 90°, derivatives]. *α*-Amino-*β*-2-furfurylaminoethane, b.p. 140—144°/17 mm. [NN'-Bz₂, m.p. 148°, -di(phenylcarbonyl), m.p. 162—163°, and -di-(*α*-naphthylcarbonyl), m.p. 183°, derivatives], is similarly obtained from (I). *αβ*-Di-*p*-methoxybenzylaminoethane (II), m.p. 30—32°, b.p. 275°/21 mm. (dihydrochloride, decomp. about 150°), and the appropriate RCHO gives 2-substituted 1:3-di-*p*-methoxybenzyltetrahydroglyoxalines in which the 2-substituent is H, m.p. 30°, *Me*, m.p. 76—77°, *Ph*, m.p. 93—94°, *p*-anisyl, m.p. 73°, 3':4'-methylenedioxyphenyl, m.p. 120°, benzyl, m.p. 68—69°, 2'-furyl, m.p. 76°, 5'-methyl-2'-furyl, m.p. 84°, and 5'-hydroxymethyl-2'-furyl, m.p. 108°. Other NN'-derivatives of (II) are: Ac₂, m.p. 151—152°, Bz₂, m.p. 182° [suitable for identification of (II)], (NO)₂, m.p. 105°, di(methylcarbonyl), m.p. 153—154°, di(phenylcarbonyl), m.p. 187°, di-2:4-dinitrophenyl, m.p. 184°, and di-2:4:6-trinitrophenyl, m.p. 205°. (II) and C₃O₂ in Et₂O at 0° give 5:7-diketo-1:4-di-*p*-methoxybenzyl-1:4-diazacycloheptane, m.p. about 90°. The dinitrate, decomp. about 100°, of (II) and abs. HNO₃ at -10° afford the dinitrate, decomp. about 150°, of *αβ*-di-(3:5-dinitro-4-methoxybenzylamino)ethane, m.p. 91—92°. *αβ*-Di-(*β'*-phenylethylamino)ethane (III), b.p. 235—240°/15 mm. (dihydrochloride, decomp. about 50°) [obtained in good yield from (·CH₂Br)₂ and CH₂Ph·CH₂·NH₂], with RCHO affords the following 2-substituted 1:3-di-*β*-phenylethyltetrahydroglyoxalines, where the 2-substituent is H, b.p. 160—180°/12 mm., *Me*, b.p. 160—190°/12 mm., *Ph*, b.p. 230—260°/21 mm., *p*-anisyl, b.p. 210—230°/15 mm., 2'-furyl, b.p. 240—255°/15 mm., and 5'-methyl-2'-furyl, b.p. 250—265°/15 mm. Other derivatives of (III) described are the Ac₂, b.p. 285—295°/12 mm., Bz₂, m.p. 194°, (NO)₂, m.p. 82—83°, di(phenylcarbonyl), m.p. 111°, di-(*α*-naphthylcarbonyl), m.p. 152—153°, di-2:4-dinitrophenyl, m.p. 187°, and di-2:4:6-trinitrophenyl, decomp. 235°. *αβ*-Diisobutylaminoethane (IV), b.p. 212° (dihydrochloride, decomp. 130°), gives with aldehydes 2-substituted 1:3-diisobutyltetrahydroglyoxalines, where the 2-substituent is H, b.p. 70—80°/28 mm., *Me*, b.p. 65—85°/28 mm., Pr^o, b.p. 90—100°/22 mm., *Ph*, m.p. 45—46°, *p*-anisyl, b.p. 130—160°/25 mm., 3':4'-methylenedioxyphenyl, m.p. 61°, 2'-furyl, b.p. 100—120°/22 mm., 5'-methyl-2'-furyl, b.p. 130—155°/22 mm., 5'-hydroxymethyl-2'-furyl, m.p. 56—57°. Other derivatives of (IV) are the Ac₂, b.p. 170—180°/20 mm., Bz₂, m.p. 127°, (NO)₂, m.p. 87°, di(phenylcarbonyl), m.p. 173—174°, di-(*α*-naphthylcarbonyl), m.p. 235°, di-2:4-dinitrophenyl, m.p. 157°, and di-2:4:6-trinitrophenyl, m.p. 196—197°. *αβ*-Di-(2-furfurylamino)ethane (V), b.p. 190°/20 mm. (dihydrochloride, decomp. about 100°), prepared by reduction of *αβ*-difurfurylideneaminoethane, m.p. 53—54°, gives with aldehydes 2-substituted 1:3-difurfuryltetrahydroglyoxalines, where the 2-substituent is H, b.p. 100—120°/24 mm., *Me*, b.p. 75—95°/18 mm., *Ph*, b.p. 190—195°/24 mm., *p*-anisyl, b.p. 220—240°/18 mm., 2'-furyl, b.p. 180—195°/20 mm., and 5'-methyl-2'-furyl, b.p. 190—210°/20 mm. Other derivatives of (V) are the Ac₂, m.p. 88°, Bz₂, m.p. 142°, (NO)₂, m.p. 79°, di(phenylcarbonyl), m.p. 174°, di-(*α*-naphthylcarbonyl), m.p. 178°,

di-2:4-dinitrophenyl, m.p. 155°, and *di*-2:4:6-trinitrophenyl, m.p. 150°. R. G.

Action of aromatic diazo-compounds on unsaturated compounds. III. A. P. TERENTIEV and A. A. DEMIDOVA (J. Gen. Chem. Russ., 1937, 7, 2464—2470).—Diallyl or $\text{CH}_2\text{:CMe}_2$ does not react at 0° with $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-N}_2\text{Cl}$ (I) or 2:4- $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-N}_2\text{Cl}$ (II). (II) with dipropenyl yields γ -2:4-dinitrobenzeneazo- $\Delta^{8,9}$ -hexadiene, m.p. 127—129° (decomp.), with $\text{CH}_2\text{:CMe:CH:CHMe}$ gives α -2:4-dinitrobenzeneazo- β -methyl- $\Delta^{8,9}$ -pentadiene, m.p. 165—167° (decomp.), with diisocrotyl affords γ -2:4-dinitrobenzeneazo- α -dimethyl- $\Delta^{8,9}$ -hexadiene, m.p. 148—151°, and with CHMe:CMe_2 yields 2:4-dinitrobenzeneazotrimethylethylene, m.p. 176—177°. (I) reacts very slowly, or not at all, with the above hydrocarbons, no product of coupling being isolated. R. T.

Azo-dyes from aryl esters of 3- and 1-hydroxy-2-naphthoic acid. E. JUSA and A. VON JANOVICH [in part with H. KRAUS and R. MELAN] (Monatsh., 1938, 71, 186—214).—Aryl esters of 3-hydroxy-2-naphthoic acid (I) are formed by the action of POCl_3 on the acid and requisite phenol. If the mixture becomes liquid below 110—120°, the ester results usually as a brown, glassy mass. If this is not the case the mixture must be liquefied below 120° by suitable addition of PhMe or xylene. The following esters are described; Ph, *p*-tolyl, 2:5-dimethylphenyl, m.p. 106—107°; *p*-chlorophenyl, m.p. 109—110° [passing if the temp. of the reaction mixture rises unduly into the chlorophenonaphthoxanthone (II), m.p. 237°]; 2:4:6-trichlorophenyl, m.p. 173°; *p*-nitrophenyl, m.p. 166°; $\alpha\text{-C}_{10}\text{H}_7$, m.p. 128—129°; $\beta\text{-C}_{10}\text{H}_7$, m.p. 143—144°; 3-carboxy-2-naphthyl, m.p. 220—221°; 1-hydroxy-2-



anthraquinonyl, m.p. 198—200°. 4':4''-Diphenylene *di*-3-hydroxy-2-naphthoate has m.p. 257—258°. Attempts to esterify (I) with picric acid gave the substance (III), m.p. 243°, which reduces $\text{NH}_3\text{-AgNO}_3$ and Fehling's solution but does not appear to react with boiling AcCl or with $\text{Ac}_2\text{O-NaOAc}$. Similarly $o\text{-OH-C}_6\text{H}_4\text{-CO}_2\text{H}$ and picric acid yielded tetrasalicylide, m.p. 263°. The following esters of 1-hydroxy-2-naphthoic acid are obtained similarly: 3:5-dimethylphenyl, m.p. 84°; *p*-chlorophenyl, m.p. 145°; 2:4:6-trichlorophenyl, m.p. 144°; *p*-nitrophenyl, m.p. 186—187°. For the production of dyes the requisite diazo-solution is added to the ester and KOH in H_2O with sufficient COMe_2 to produce a clear solution. Thus are obtained Ph 3-hydroxy-4-4'-sulphobenzeneazo-2-naphthoate and the corresponding *p*-tolyl, decomp. 273—274°, 3:5-dimethylphenyl, decomp. 269°, *p*-chlorophenyl, decomp. 278°, 2:4:6-trichlorophenyl, decomp. 276°, *p*-nitrophenyl, $\alpha\text{-C}_{10}\text{H}_7$, $\beta\text{-C}_{10}\text{H}_7$, and 1-hydroxy-2-anthraquinonyl esters. 3:5-Dimethylphenyl 1-hydroxy-4-4'-sulphobenzeneazo-2-naphthoate and the corresponding *p*-chlorophenyl, 2:4:6-trichlorophenyl and *p*-nitrophenyl esters are described. The tinctorial properties of the above dyes and the

products of the coupling of aryl hydroxynaphthoates with diazotised naphthionic acid, $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH}_2$, benzidine, or dianisidine are described. H. W.

Aminoarylhydrazinesulphonic acids.—See B., 1938, 255.

Solid diazonium salts.—See B., 1938, 255.

Reaction of 1-chloro- β -naphthol with *p*-nitrobenzenediazonium salts. J. S. JOFFE (J. Gen. Chem. Russ., 1937, 7, 2637—2638).—1:2- $\text{C}_{10}\text{H}_6\text{Cl-OH}$ and diazotised $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH}_2$ in aq. NaOAc , $\text{Na}_2\text{S}_2\text{O}_3$, or NaOH yield a red diazo-ether, m.p. 125° (decomp.), probably $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-N}_2\text{-O-C}_{10}\text{H}_6\text{Cl}$. R. T.

[4-Nitronaphthalenediazoaminobenzene-4'-azobenzene, m.p. 175° (decomp.); benzenediazoaminobenzene-4-azo-4'-nitrobenzene, m.p. 191° (decomp.)].—See A., 1938, I, 213.

Action of nitrous acid on the bromine substitution products of phenols. L. C. RAIFORD and J. H. SCOTT (J. Org. Chem., 1937, 2, 213—221).—2:4:6-Tribromo-3:5-dimethylphenol with AcOH-NaNO_2 gives 2:6-dibromo-4-nitro-3:5-dimethylphenol (I), decomp. 172—173°, and 2:6-dibromo-3:5-dimethyl-*p*-benzoquinone, m.p. 172°, reduced by SnCl_2 to the quinol, decomp. about 211° (Ac_3 , m.p. 215—216°, and Bz_2 , m.p. 249—250°, derivatives). (I) is reduced by $\text{SnCl}_2\text{-HCl-AcOH}$ to 2:6-dibromo-4-amino-3:5-dimethylphenol, m.p. 207° (decomp.) (hydrochloride; N-Ac , m.p. 243—244°, O-Bz-N-Ac , m.p. 252—253°, ON-Bz_2 , m.p. >276°, N-Bz , m.p. 257—258°, N-Bz-O-Ac , m.p. 210°, ONN-Ac_3 , m.p. 153—154°, derivatives). The existence of two isomeric Bz-Ac derivatives which did not rearrange on hydrolysis indicates that the substance is not an *o*-aminophenol (cf. A., 1934, 1012), whereby the structure is proved. 2:4:6-Tribromo-3-methoxyphenol, new m.p. 104—105°, with AcOH-NaNO_2 gives 2:4-dibromo-6-nitro-3-methoxyphenol, m.p. 126—127° (cf. lit.), reduced to 2:4-dibromo-6-amino-3-methoxyphenol, m.p. 105—106.5° [hydrochloride; N-Ac , m.p. 157—158°, N-Bz (II), m.p. 146—147°, ON-Bz_2 , m.p. 169—170°, N-Bz-O-Ac , m.p. 170—171°, O-Bz-N-Ac (III), m.p. 186—186.5°, derivatives]. Hydrolysis of (III) causes rearrangement and gives (II), and this confirms the constitution given. H. G. M.

[Aryl]sulphonates of phenylphenols. S. E. HAZLET (J. Amer. Chem. Soc., 1938, 60, 399—400).—The *p*-bromo-, m.p. 69—70°, 102.5—103.5°, and 185—186°, *o*-, m.p. 72—73°, 69—70°, and 138—139°, *m*-, m.p. 130—131°, 111—112°, and 143—144°, and *p*-nitrobenzenesulphonates, m.p. 110—111°, 97—98°, and 148.5—149.5°, of 2-, 3-, and 4-hydroxydiphenyl, respectively, are prepared. R. S. C.

Syntheses in the phenanthrene series. VIII. 8-Methoxy-1-methylphenanthrene. P. HILL, W. F. SHORT, and H. STROMBERG (J.C.S., 1937, 1619—1622; cf. A., 1937, II, 337).—The Grignard reagent from β -*o*-anisylethyl chloride, b.p. 117—119°/8 mm. (prep. from PhOH through $o\text{-C}_6\text{H}_4\text{Br-OH}$, $o\text{-C}_6\text{H}_4\text{Br-OMe}$, and $o\text{-C}_6\text{H}_4\text{OMe-CH}_2\text{-CH}_2\text{-OH}$ described), and 2-methylcyclohexanone afford 1- β -*o*-anisylethyl-2-methylcyclohexanol, b.p. 175—176°/7 mm., dehydrated with KHSO_4 to 1- β -*o*-anisylethyl-2-methyl-

cyclohexene, b.p. 155—156°/6 mm. This when treated with AlCl_3 and the product dehydrogenated with S gives 8-methoxy-1-methylphenanthrene (I), m.p. 96—97° (picrate, m.p. 141.5—142.5°), demethylated by $\text{HBr}-\text{AcOH}$ to 8-hydroxy-1-methylphenanthrene, m.p. 144—145°. Reduction of 1:5- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NO}_2$ with Zn and NH_4Cl gives 1:5- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NH}_2$ and 5:5'-dibromo- α -azoxynaphthalene, m.p. 211.5—212° (decomp.). The former by improved methods leads to 1:5- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{OMe}$, the Grignard compound of which with succinic anhydride in C_6H_6 gives β -5-methoxy-1-naphthylpropionic acid, m.p. 153.5—154°, reduced (Clemmensen) to γ -5-methoxy-1-naphthylbutyric acid (II), which with boiling $\text{HBr}-\text{AcOH}$ affords γ -5-hydroxy-1-naphthylbutyric acid (III), m.p. 155—156°. (III) with SnCl_4 , or better with $\text{P}_2\text{O}_5-\text{C}_6\text{H}_6$, affords 1-keto-8-methoxy-1:2:3:4-tetrahydrophenanthrene, m.p. 88—89° [2:4-dinitrophenylhydrazones, m.p. 250—251° (decomp.); semicarbazones, m.p. 221° (decomp.)], but no compound, m.p. 137°, was obtained (cf. Kon et al., A., 1936, 465). With boiling $\text{HBr}-\text{AcOH}$ this ketone gives (III), fission of the hydroaromatic ring taking place, and with MgMeI gives 8-methoxy-1-methyl-3:4-dihydrophenanthrene, m.p. 104—105°, and an oil which is dehydrogenated ($\text{Pd}-\text{C}$) to (I).

H. G. M.

Rearrangement of fluorylidene dimethyl sulphide [dimethylsulphonium 9-fluorenylidide] to 1-fluorenylmethyl methyl sulphide. G. E. HILBERT and L. A. PINCK (J. Amer. Chem. Soc., 1938, 60, 494).— $\text{C}_6\text{H}_4 > \text{C}^+\text{SMe}_2$ (Ingold and Jessop, A., 1930, 759) in $\text{NaOH}-\text{EtOH}$ or liquid NH_3 gives 1-fluorenylmethyl Me sulphide, oxidised by H_2O_2 to the corresponding sulphone, or by $\text{K}_2\text{Cr}_2\text{O}_7$ to 1-fluorenylmethyl Me sulphone and fluorenone-1-carboxylic acid, and converted by $\text{HCl}-\text{MeOH}$ into 1-methoxymethylfluorene or by $\text{HBr}-\text{AcOH}$ into 1-bromomethylfluorene (reduced by $\text{Zn}-\text{AcOH}$ to 1-methylfluorene).

R. S. C.

Sulphonium compounds. I. Mechanism for the reaction of organic halides with sulphides. F. E. RAY and I. LEVINE (J. Org. Chem., 1937, 2, 267—275).—In all reactions between org. halides and sulphides the primary product is a sulphonium salt. According to its complexity this may decompose in one, two, or three ways giving halides and sulphides which, in turn, can combine to form the same or other sulphonium salts. The tendency is for that salt having the smallest org. radicals to be the final product of the reaction. Ph 2-fluoryl ketone, m.p. 122°, is reduced by Zn dust and NH_3-EtOH or $\text{KOH}-\text{EtOH}$ to phenyl-2-fluorylcarbinol, m.p. 116°, which gives phenyl-2-fluorylmethyl chloride, m.p. 122°, and bromide (I), m.p. 118.5°, when treated with the requisite halogen acid in AcOH . KI and (I) give much I and s-diphenyldi-2-fluorylethane (II), m.p. 284—285°, whereas MeI slowly converts (I) into phenyl-2-fluorylmethyl iodide, m.p. 126—127°. Boiling MeOH and (I) give phenyl-2-fluorylcarbinyl Me ether, m.p. 92°, the Et, m.p. 80°, Pr^a , m.p. 53°, and Bu^a , m.p. 68°, ethers being obtained similarly. Boiling EtSH and (I) yield phenyl-2-fluorylmethyl Et sulphide, m.p. 68—70°; the Pr^a and Bu^a sulphides have m.p. 51° and m.p. 81°, respectively.

E ** (A., II.)

Na wire and (I) in boiling anhyd. Et_2O give (II) and its diastereoisomeride (III), m.p. 168°. Ph phenyl-2-fluorylmethyl sulphide, from (I) and PhSH , has m.p. 149°. Me_2S and (I) give SMe_3Br , m.p. 200°, and phenyl-2-fluorylmethyl Me sulphide, m.p. 109.5°. This when kept with an excess of MeI gives SMe_3I and (III).

H. W.

Mobility of groups containing a sulphur atom.

IV. D. T. GIBSON (J.C.S., 1937, 1509—1512; cf. A., 1937, II, 183).—The reaction between Me d-camphorthiolsulphonate (prep. described) and a series of reactive methylene compounds at 20° has been followed polarimetrically. In the reaction $\text{CH}_2\text{XY} + \text{RS}\cdot\text{SO}_2\text{R}' \rightarrow \text{CHXY}\cdot\text{SR} + \text{R}'\cdot\text{SO}_2\text{Na}$. (X, Y are activating CO or SO_2 radicals), $\text{R}'\text{SO}_2$ becomes an anion and RS functions transiently as cation which combines with the CH_2 anion. In accord with this view the reaction is favoured by increasing alkalinity, by a group R which increases the acceptor tendency of RS, and by use of thiolsulphonic esters which liberate a relatively strong sulphonic acid ($2:5\text{-C}_6\text{H}_3\text{Cl}_2\cdot\text{SO}_2\cdot\text{S}\cdot\text{C}_6\text{H}_3\text{Cl}_2 > p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\cdot\text{S}\cdot\text{C}_6\text{H}_3\text{Cl}_2 > p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{S}\cdot\text{C}_6\text{H}_3\text{Cl}_2$). The effect of the groups activating the CH_2 is discussed with respect to enolisation, optimum activation, and a pseudo-reversibility which gives the appearance of incomplete reaction. $\text{PhSO}_2\cdot\text{CH}_2\cdot\text{COPh}$ with excess of MeSO_2Cl and alkali gives (benzenesulphonyl)-(methanesulphonyl)benzoylmethane, m.p. 166°, and d-camphorsulphonyl chloride with $\text{CH}_2(\text{SO}_2\text{Et})_2$ gives camphorsulphonylbisethanesulphonylmethane, m.p. 213°. PhSO_2Cl with $\text{MeSO}_2\cdot\text{CH}_2\cdot\text{COMe}$ gives diphenyldisulphone and with $\text{CH}_2(\text{SO}_2\text{Et})_2$, dichlorobisethanesulphonylmethane, m.p. 98° (incorrectly reported as Cl-derivative; A., 1931, 1394).

H. G. M.

Diaryls and their derivatives. XV. Reactions of β -naphthol-3:6-disulphonic acid with ferric salts. J. S. JOFFE and E. TSCHERNISCHEVA. **XVI. Reaction of β -naphthol-5-sulphonic and -5:7-disulphonic acid with ferric salts.** J. S. JOFFE and V. I. KOBJAKOVA. **XVII. Reaction of β -naphthol-4-sulphonic acid and its derivatives with ferric salts.** J. S. JOFFE and M. A. BENIDIKTOVA-FLEISCHER (J. Gen. Chem. Russ., 1937, 7, 2398—2401, 2457—2460, 2678—2680).—XV. 2:3:6- $\text{OH}\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{Na})_2$ in neutral or acid solution and FeCl_3 yield 2:1:3:6- $\text{OH}\cdot\text{C}_{10}\text{H}_4\text{Cl}(\text{SO}_3\text{H})_2$ (I) and 2:2'-dihydroxy-1:1'-dinaphthyl-3:6:3':6'-tetrasulphonic acid (II) (Na salt); (I) is the sole product in 43% HCl , and (II) in presence of $\text{Fe}_2(\text{SO}_4)_3$. The Cl of (I) is not replaced by heating with aq. NH_3 , NH_2Ph , or KOH , but is readily eliminated by AgNO_3 in dil. aq. HNO_3 , or by $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{HSO}_4$.

XVI. 2:5- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ and FeCl_3 in neutral or HCl solution (at the b.p.) afford 2:2'-dihydroxy-1:1'-dinaphthyl-5:5'-disulphonic acid (Na salt). 2:5:7- $\text{OH}\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_2$ reacts analogously to the 3:6-acid, to yield 2:2'-dihydroxy-1:1'-dinaphthyl-5:7:5':7'-tetrasulphonic acid and 1-chloro- β -naphthol-5:7-disulphonic acid.

XVII. β -Naphthol-4-sulphonic acid and FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$ yield 2:2'-dihydroxy-1:1'-dinaphthyl-4:4'-disulphonic acid (Na and quinine salts). 6-Nitro- β -

naphthol-4-sulphonic acid and FeCl_3 afford only 1-chloro-6-nitro- β -naphthol-4-sulphonic acid. R. T.

Additive compounds of pyrocatechol. (MLLE.) Y. GARREAU (Compt. rend., 1938, 206, 439—441; cf. A., 1934, 1346).— $o\text{-C}_6\text{H}_4(\text{OH})_2$ with SO_2 , $(\text{CH}_2\cdot\text{NH}_2)_2$, and the metal hydroxide affords (cf. A., 1938, II, 96) compounds, $2\text{C}_6\text{H}_4(\text{OH})_2\cdot(\text{CH}_2\cdot\text{NH}_2)_2\cdot\text{X}$ [$\text{X} = \text{Cu}(\text{H}_2\text{O})$, Ni, and Zn], and the substance $5\text{C}_6\text{H}_4(\text{OH})_2\cdot 3(\text{CH}_2\cdot\text{NH}_2)_2\cdot 2\text{Cd}\cdot\text{CdSO}_3$. Electrolysis of the compound $m\text{-C}_6\text{H}_4(\text{OH})_2\cdot 2(\text{CH}_2\cdot\text{NH}_2)_2\cdot\text{CuSO}_3\cdot\text{H}_2\text{O}$, shows that $m\text{-C}_6\text{H}_4(\text{OH})_2$ does not form part of the cation. J. L. D.

Comparative reducing power of various phenols. A. IONESCO-MATIU and A. POPESCU (J. Pharm. Chim., 1938, [viii], 27, 193—203).—The amounts of Ag liberated from $\text{NH}_3\text{-AgNO}_3$ by various phenols at 20° , 37° , and 50° are determined. The following relative reducing powers are deduced: $m\text{-} < p\text{-} < o\text{-C}_6\text{H}_4(\text{OH})_2 < \text{phloroglucinol} < \text{pyrogallol} < \text{gallic acid}$; $\beta\text{-} < \alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$. Naphthyl benzoates have little reducing power until hydrolysed.

R. S. C.

Action of thiochronic and 2 : 5-dichloroquinol-3 : 6-disulphonic acids on primary amines. Constitution of the latter acid and of euthiochronic acid. (MLLE.) Y. GARREAU (Compt. rend., 1938, 206, 256—258).—K 2 : 5-dichloroquinol-3 : 6-disulphonate (I) with cyclohexylamine (II) affords cyclohexylammonium 2 : 5-di(cyclohexylamino)benzoquinone-3 : 6-disulphonate (III) (cf. A., 1937, II, 251), converted by dil. HCl into 2 : 5-di(cyclohexylamino)benzoquinone, which establishes the constitution of (I). (III) with dil. KOH affords K 4 : 4-dihydroxy-1-keto-3 : 6-dipotassiumoxy-1 : 4-dihydrobenzene-2 : 5-disulphonate (K euthiochronate). K thiochronate (K 4-hydroxy-1-keto-1 : 4-dihydrobenzene-2 : 3 : 4 : 5 : 6-pentasulphonate) with warm (II) affords (III).

J. L. D.

Addition of chloroform and bromoform to *m*-chlorobenzaldehyde and *p*-tolualdehyde. J. W. HOWARD and G. N. STEPHENS (J. Amer. Chem. Soc., 1938, 60, 228—229).— $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ with CHHal_3 and solid KOH gives *m*-chlorophenyltrichloromethylcarbinol, b.p. $182\text{—}182^\circ/24\text{ mm.}$ (acetate, m.p. $59\text{—}60^\circ$; propionate, b.p. $172\text{—}173^\circ/12\text{ mm.}$; butyrate, b.p. $183\text{—}184^\circ/10\text{ mm.}$; benzoate, m.p. $92\text{—}93^\circ$), *m*-chlorophenyltribromomethylcarbinol, b.p. $207\text{—}208^\circ/12\text{ mm.}$ (acetate, m.p. $100\text{—}101^\circ$; propionate, m.p. $61\text{—}62^\circ$; butyrate, b.p. $193^\circ/25\text{ mm.}$; benzoate, m.p. $114\text{—}115^\circ$), *p*-tolyltrichloromethylcarbinol, b.p. $155\text{—}157^\circ/8\text{ mm.}$, m.p. $58\text{—}59^\circ$ (acetate, m.p. $105\text{—}106^\circ$; propionate, m.p. $59\text{—}60^\circ$; butyrate, b.p. $172\text{—}173^\circ/11\text{ mm.}$; benzoate, m.p. $94\text{—}95^\circ$), and *p*-tolyltribromomethylcarbinol, m.p. $61\text{—}62^\circ$, b.p. $183\text{—}186^\circ/4\text{ mm.}$ (acetate, m.p. $149\text{—}150^\circ$; propionate, m.p. 170° ; butyrate, m.p. 63° ; benzoate, m.p. 126°), respectively. R. S. C.

Reactions between some phenol alcohols and fatty acid esters. S. KITaura (Bull. Inst. Phys. Chem. Res. Japan, 1937, 16, 1454—1463).—The equilibrium consts. for alcoholysis [K_2CO_3 or $\text{Al}(\text{OEt})_3$ as catalyst] of EtOAc by $\text{CH}_2\text{Ph}\cdot\text{OH}$ and $\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{OH}$ at 85° are 0.27 and 0.41, respectively. *o*-Hydroxyphenylpropyl palmitate, m.p. $58\text{—}59^\circ$,

stearate, m.p. $64.5\text{—}65.5^\circ$, oleate ($4'\text{-iododiphenylurethane}$, m.p. $67\text{—}68^\circ$), and linolenate were prepared by alcoholysis of the Et esters. A. Lr.

Polymorphism of *p*-tolyl triphenylmethyl ether. J. VAN ALPHEN (Ber., 1938, 71, [B], 491).—In reply to Funakubo *et al.* (A., 1937, II, 57) it is pointed out that the compound, m.p. 81° , of van Alphen (A., 1927, 660) is not $\text{CPh}_3\cdot\text{OEt}$ but is one form of the trimorphous $\text{CPh}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{p}$. H. W.

Analytical reactions of ephedrine. New methods for its identification. M. PESEZ (J. Pharm. Chim., 1938, [viii], 27, 120—128).—Most colour reactions for ephedrine are not sp. With $\text{CH}_2\text{O}\text{—H}_2\text{SO}_4$ it gives a pink to blood-red colour, and by nitration and subsequent treatment with $\text{COMe}_2\text{—NaOH}$ a red colour, both reactions being due to the C_6H_5 ring. With NaOBr it gives CHBr_3 , identified by the red colour given with $\text{C}_5\text{H}_5\text{N}\text{—NaOH}$.

R. S. C.

Elimination of the amino-group from tertiary amino-alcohols. IX. Semipinacolic deamination of isomeric α - and β -amino-alcohols. A. MCKENZIE and A. D. WOOD (Ber., 1938, 71, [B], 358—365; cf. A., 1930, 778).—Addition of $r\text{-NH}_2\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2$ to $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ in Et_2O gives *r*-*p*-tolyl α -aminobenzyl ketone [hydrochloride (I), m.p. $230\text{—}232^\circ$; 2 : 4-dinitrophenylhydrazones, m.p. $184\text{—}186^\circ$ (sulphate, m.p. $194.5\text{—}195^\circ$)], also obtained from *dl*-aminophenylacetyl [chloride hydrochloride (from $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, AcCl , and PCl_5) by means of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ or AlCl_3 and PhMe at -2° . (I) and MgPhBr give *r*- β -amino- $\alpha\beta$ -diphenyl- α -*p*-tolyl-ethanol (β -variety), m.p. $154\text{—}155^\circ$ (hydrochloride, m.p. $227\text{—}227.5^\circ$), converted by HNO_2 into *p*-tolyl benzhydryl ketone, m.p. $99\text{—}100^\circ$. β -Benzilmonoxime (II) and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$ yield *r*- β -oximino- $\alpha\beta$ -diphenyl- α -1-naphthylethanol, reduced by $\text{Na}\text{—Hg}$ in warm $\text{MeOH}\text{—AcOH}$ to a mixture of β -amino- $\alpha\beta$ -diphenyl- α -1-naphthylethanols, α -form, m.p. $197\text{—}198^\circ$, and β -variety, m.p. $156\text{—}157^\circ$; the latter is deaminated to *r*-1-naphthyldeoxybenzoin, m.p. $106\text{—}107^\circ$. In this case the C_{10}H_7 group is more mobile than Ph, whereas the reverse is the case with the α -form. *r*-Desylamine hydrochloride and $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ give *r*- β -amino- $\alpha\beta$ -diphenyl- α -*o*-tolyl-ethanol (α -form), m.p. $136\text{—}137.5^\circ$ (hydrochloride, m.p. $220\text{—}221^\circ$), deaminated to *o*-tolyl benzhydryl ketone, m.p. $47\text{—}48.5^\circ$. $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ and (II) give *r*-*o*-tolyl- α -benzoinoxime (III), m.p. $181.5\text{—}182.5^\circ$; the change in configuration during the reaction is established by its production from α -benzilmonoxime and by the formation of a pale green complex compound with $\text{Cu}(\text{NO}_3)_2$. Reduction of (III) in $\text{MeOH}\text{—COMe}_2\text{—AcOH}$ affords *r*- β -amino- $\alpha\beta$ -diphenyl- α -*o*-tolyl-ethanol (β -form), m.p. $153\text{—}154^\circ$ (hydrochloride, m.p. $223\text{—}224^\circ$), which with HNO_2 gives non-cryst. material. H. W.

Rearrangement of styryl-substituted ethanes. C. S. MARVEL, M. B. MUELLER, and W. J. PEPPEL (J. Amer. Chem. Soc., 1938, 60, 410—413).— $\text{CHPh}\cdot\text{CH}\cdot\text{CPh}_2\cdot\text{OH}$ and VCl_3 in AcOH give, by $\alpha\gamma$ -change of $\text{CHPh}\cdot\text{CH}\cdot\text{CPh}_2$, $\alpha\gamma\delta\zeta$ -hexaphenyl- $\Delta^{\alpha\alpha}$ -hexadiene (I), m.p. $210\text{—}211^\circ$, also obtained by $\text{HCl}\text{—AcOH}$ from $\alpha\gamma\delta\zeta$ -hexaphenyl- $\alpha\zeta$ -diol, m.p. 193—

194°, which is prepared from Me_2 meso- $\beta\beta'$ -diphenyl-adipate and LiPh . LiCH:CHPh and CO(CH:CHPh)_2 give *tristyrilcarbinol*, m.p. (+ H_2O) 110–111°, (anhyd.) 120.5–121°, which with VCl_3 gives a red solution, probably containing $(\text{CHPh:CH})_3\text{C}$, and then a stable, colourless *hydrocarbon*, (?) $[(\text{CHPh:CH})_2\text{C:CH-CHPh}]_2$ m.p. 173–174°, which is analogous to (I), gives alkali metal additive compounds at the ethylenic linking, and with O_3 gives BzOH and resins. R. S. C.

Condensations by sodium. XI. Trimethoxy-trixenylcarbinol. Comparisons of colours of some carbonium salts in this series. A. A. MORTON and W. S. EMERSON (J. Amer. Chem. Soc., 1938, 60, 284–285; cf. A., 1938, II, 8, 57).—4-Bromo-4'-methoxydiphenyl, Et_2CO_3 , and Na in C_6H_6 give 27.5% of *tri-(4'-methoxy-p-diphenyl)carbinol*, m.p. 188–189°. With $(p\text{-C}_6\text{H}_4\text{R}\cdot\text{C}_6\text{H}_4)_3\text{C-OH}$, the order of intensity of colour in $\text{AcOH-H}_2\text{SO}_4$ is $\text{R} = \text{OMe} > \text{Me} > \text{H}$, as in the $\text{CPh}_3\text{-OH}$ series, but all compounds of the latter series are less coloured.

R. S. C.

Derivatives of *cyclopentanoperhydrophenanthrene*. U. SANTI (Boll. Chim. Farm., 1938, 77, 113–128).—A review.

Molecular rearrangements in the sterols. III. Constitution of *i*-cholesterol and of the isomeric ethers of cholesterol. E. G. FORD, P. CHAKRAVORTY, and E. S. WALLIS (J. Amer. Chem. Soc., 1938, 60, 413–415; cf. A., 1937, II, 416).—Wallis' formula (A., 1937, II, 99) for *i*-cholesterol is confirmed by isolation of *i*-cholestanone, m.p. 110–111°, $[\alpha]_D^{25} +64.9^\circ$ in CHCl_3 , and conversion of this by AcOH-HCl into α -3-chlorocholestan-6-one.

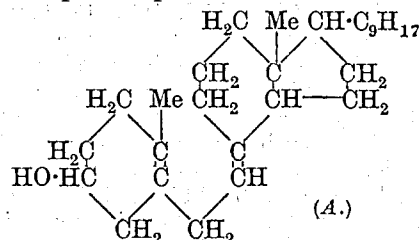
R. S. C.

Attempted preparation of 7:8-dehydrocholesterol through a 7-amincholesterol. H. J. ECKHARDT (Ber., 1938, 71, [B], 461–470).—7-Ketocholesteryl acetate is converted into the *oxime* (I), m.p. 184°, $[\alpha]_D^{25} -196^\circ$ in CHCl_3 , hydrolysed to *cholesterol-7-ketoxime*, m.p. 235° (decomp.). Reduction of (I) with Na and EtOH gives 7-amincholesterol (II), a mixture of stereoisomerides, m.p. (indef.) 167–170° [*hydrochloride*, m.p. 270–280° (decomp.)], $[\alpha]_D^{25} -20^\circ$ to -6° in MeOH ; *phosphate* (III), $\text{C}_{27}\text{H}_{47}\text{ON}_2\text{H}_3\text{PO}_4\cdot\text{H}_2\text{O}$, m.p. 277–280° (decomp.); *sulphate*, m.p. 145° with violet coloration; *borate*, m.p. 260–265° (decomp.); *oxalate*, m.p. 210–215° (decomp.)]. Ac_2O and (II) in Et_2O afford α -, m.p. 290° (decomp.), and β -, m.p. 266–268°, 7-acetamidcholesterol, separable by the differing solubility in EtOH . With Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 100° (II) yields 7-acetamidcholesteryl acetate, m.p. 210°, $[\alpha]_D^{25} +49.7^\circ$ in CHCl_3 , the double linking in which is established by micro-hydrogenation. (II) is transformed by Bz_2O in boiling C_6H_6 into 7-benzamidcholesterol, m.p. 240°, and by BzCl in $\text{C}_5\text{H}_5\text{N}$ at room temp. into 7-benzamidcholesteryl benzoate, m.p. 252–253°, $[\alpha]_D^{25} +96.5^\circ$ in CHCl_3 . With MeI in Et_2O at room temp. (II) affords 7-methylamincholesterol hydriodide, m.p. 249–251°; the corresponding free base is converted by MeI into 7-dimethylamincholesterol, m.p. 160° [isolated as the *oxalate* (+ $2\text{H}_2\text{O}$), m.p. 184° (decomp.)], which does not react with MeI ; it is formed directly by the action of KOH and MeI in boiling MeOH on

(II). Thermal decomp. of (III) yields a *cholesta-triene* (IV) $\text{C}_{27}\text{H}_{42}$, m.p. 67–69°, $[\alpha] \pm 0^\circ$; the behaviour of other derivatives is described. 7-Hydroxycholesterol and Bz_2O in boiling C_6H_6 , PhMe , or xylene give 7-hydroxycholesteryl 3-benzoate, b.p. 225–230°/high vac., m.p. 192° from abs. EtOH or 184° from $\text{MeOH-H}_2\text{O}$, $[\alpha]_D^{25} +13.8^\circ$ in CHCl_3 , converted by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 100° into the corresponding 7-acetate, m.p. 149°, and partly dehydrated by KH_2PO_4 at 200°/high vac. to BzOH and (IV).

H. W.

Constitution of vitamin- D_2 . K. VON AUWERS (Annalen, 1938, 533, 255–263).—Cholesterol with one double linking and a series of other compounds of the group show a distinct depression of n and a slightly increased dispersive power which is thus characteristic of four-ring systems of this type. Suprasterol I and II and the acetate of the former, with three isolated double linkings, behave similarly. Ergosterol, its acetate, palmitate, and benzoate containing a simple conjugation show slight increase of n and markedly increased dispersion. In dehydroergosteryl acetate (I) n and dispersive power are further increased in



harmony with the formula of Windaus and Thiele (A., 1936, 69). The optical behaviour of dihydrovitamin does not indicate conclusively the presence or absence of conjugation but the close similarity to the suprasterols and the absence of characteristic bands in the absorption spectrum confirm the constitution (A) from the physical side. The optical behaviour of vitamin- D_2 (II) confirms the Windaus formula (*loc. cit.*) with accumulated conjugation and definitely excludes that of Rudy with doubly broken single conjugation. Since the increase in n is greater with (II) than with (I) the presence of two semicyclic double linkings in (II) is established since such linkings have a greater effect than those of the usual type. Examination of the 3:5-dinitro-*p*-toluates of suprasterol II, (II), and tachysterol (III) shows the presence in (III) of three double linkings in accumulated conjugation but the absence of semicyclic linkings, thus harmonising with the structures suggested by Lettré (A., 1934, 887). *Et* 3:5-dinitro-*p*-toluate, m.p. 74–75°, is described incidentally. H. W.

Vitamin-E. III. Structure of α - and β -tocopherol. F. BERGEL, A. R. TODD, and T. S. WORK (J.C.S., 1938, 253–258; cf. A., 1938, III, 133).—Crude β -tocopheryl allophanate (I), m.p. 138°, is separated by MeOH-charcoal into pure (I), m.p. 143.5–144.5°, and a little β -amyrin allophanate, m.p. 273–275°. Both (I) and β -tocopherol (II) with H_2 - PtO_2 absorb 4 H. Oxidation of (I) with $\text{KMnO}_4\text{-NaOH}$ in hexane yields an oily acid (*p*-phenylphenacyl ester, m.p. 84°). Pyrolysis of active concentrates of wheat-germ oil at 350–360° yields duroquinol (III) [*mono*-,

m.p. 98°, and *di*-, m.p. 81–84° (turbid; clear at 86–87°), *cetyl ethers*; *monobenzoate*, m.p. 221–223° (*allyl ether*, m.p. 111–112°); *monoallyl ether*, m.p. 108° and *p*-cymoquinol. (III) is formed by pyrolysis of its *cetyl ethers*. Absorption spectra of (I), (II), and the ethers of (III) are given; crystallographic data for (I) indicate a C_{30} structure, and therefore a C_{28} structure for (II). Cumotocopherol (John, A., 1937, III, 497) and neotocopherol (Karrer *et al.*, A., 1938, II, 13) are probably identical with (II). J. D. R.

Phytosterol in wheat-germ oil. II. A. ICHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, 34, 116–120; cf. A., 1935, 1551).— Al_2O_3 adsorbs from a light petroleum solution of the sterols from wheat-germ oil a *substance*, m.p. 74–75°, responsible for certain characteristic absorption bands. Fractionation of the sterol benzoates yields α - and β -tritosterols and a sterol, m.p. 162–163°, $[\alpha]_D^{20} +98.3^\circ$ in $CHCl_3$ (*benzoate*, m.p. 170–171°, $[\alpha]_D^{20} +110.4^\circ$ in $CHCl_3$), possibly identical with that obtained by Karrer and Solomon (A., 1937, II, 242). A. LI.

Purification of sitosterol. A. CASTILLE and E. RUPPOL (Bull. Soc. Chim. biol., 1937, 19, 1716–1730).—Bromination is unsatisfactory as a method of purification of sitosterol, since it introduces dihydro-sitosterol as a new impurity on removal of Br by Zn and AcOH. By a combination of benzoylation and acetylation, followed by repeated crystallisation from EtOH, a dextrorotatory impurity is removed and (γ)-sitosterol, m.p. 146–147.5°, $[\alpha]_D -45.86^\circ$, is obtained. The existence of three isomeric sitosterols (cf. Anderson *et al.*, B., 1927, 48, 49) is doubted.

P. G. M.

Stereochemistry of acenaphthylene and tetrahydroacenaphthylene glycols. I. (Miss) K. M. JACK and H. G. RULE (J.C.S., 1938, 188–192).—*trans*-Acenaphthylene glycol (I) with *l*-menthoxyacetyl chloride in C_5H_5N yields *d*-*trans*-acenaphthylene glycol *di-l*-menthoxyacetate, m.p. 114–115°, $[\alpha]_{461}^{20} -327.3^\circ$ in C_6H_6 , hydrolysed by EtOH–NaOH to *d*-*trans*-acenaphthylene glycol, m.p. 158–158.5°, $[\alpha]_{461}^{20} +66^\circ$ in C_6H_6 , $+52^\circ$ in $CHCl_3$, 0° in EtOH or MeOH, -25° in CO_2Et , and -76° in $PhNO_2$. Similarly from *cis*-acenaphthylene glycol (II) is formed *cis*-acenaphthylene glycol *di-l*-menthoxyacetate, m.p. 40–42°, $[\alpha]_{461}^{20} -114.8^\circ$ in C_6H_6 , hydrolysed to (II). Reduction (Na–Hg–EtOH) of acenaphthenequinone (III) yields *trans*-1:2:3:4-tetrahydroacenaphthylene glycol, m.p. 208.5–209° (*diacetate*, m.p. 139–140°; *di-l*-menthoxyacetate, m.p. 71–72°, $[\alpha]_{461}^{20} -96^\circ$ in C_6H_6), also formed by catalytic reduction (H_2 , PtO_2 , EtOH–HCl– $FeCl_3$) of (I). Catalytic reduction of (II) and (III) yields *cis*-1:2:3:4-tetrahydroacenaphthylene glycol, m.p. 92.5–93.5° (*isopropylidene ether*, m.p. 51–52°; *diacetate*, m.p. 121–121.5°), and a mixture of (I) and (II), respectively.

J. D. R.

α -Phenylthiolpropionic acid. L. RAMBERG and I. HEDLUND (Arkiv Kemi, Min., Geol., 1937, 12, A, No. 12, 9 pp.).— α -Phenylthiolpropionic acid, b.p. 168–170°/9 mm.; m.p. 20.6–20.7° [*Na*, $+H_2O$, and *Ba*, $+5H_2O$, salts; *amide*, m.p. 117–117.6° (corr.); dimethylamide, an oil], obtained in 85% yield from $PhSNa$, $CHMeBr \cdot CO_2Na$, and aq. NaOH, is best

resolved by quinine, giving the *d*- (*amide*, m.p. 145.9–146.5°, $[\alpha]_D^{25} +93^\circ$, $[\alpha]_{461}^{25} +115^\circ$ in 95% EtOH; dimethylamide, oil, $[\alpha]_{461}^{25} +86^\circ$ in 95% EtOH) and *l*-forms, $[\alpha]_D^{25} \pm 117^\circ$ to $\pm 123.4^\circ$ in H_2O (according to the concn.). The rate of racemisation in aq. NaOH in presence of a little $PhSNa$ in N_2 is $\propto [OH^-]$ and independent of the $[PhSNa]$.

R. S. C.

Michael reaction. II. Nature of the condensation product from ethyl benzylmalonate and ethyl fumarate. J. A. GARDNER and H. N. RYDON (J.C.S., 1938, 42–45; cf. A., 1935, 977).—Condensation of $CH_2Ph \cdot CH(CO_2Et)_2$, b.p. 140–140.5°/1.5 mm., with $CHBr(CO_2Et) \cdot CH_2 \cdot CO_2Et$, b.p. 136–138°/17 mm., and with Et fumarate gives respectively Et δ -phenyl-*n*-butane- $\alpha\beta\gamma$ -tetracarboxylate (I), b.p. 205–207°/1.3 mm., and - $\alpha\beta\gamma$ -tetracarboxylate (II), b.p. 198–200°/0.9 mm. (cf. A., 1935, 977; Duff and Ingold, *ibid.*, 976), both giving on hydrolysis different proportions of two stereoisomeric α -benzyltricarballic acids (cf. Malachowski, A., 1936, 967). NaOEt converts (I) into (II), as shown by identity of the hydrolysis products. E. G. B.

Michael reaction. IV. Addition of alkylmalonic esters to α -substituted Δ^4 -unsaturated esters: general conclusions. J. A. GARDNER and H. N. RYDON (J.C.S., 1938, 48–55).— $CHMe(CO_2Et)_2$ (I) with Et Δ^4 -tetrahydrobenzoate, b.p. 95–97°/15 mm., in EtOH–NaOEt (1 equiv.) gives $\approx 6\%$ of the normal product, viz., Et (2-carbethoxycyclohexyl)methylmalonate, b.p. 158–160°/1.5 mm. [synthesised (b.p. 164–166°/3 mm.) from Et sodio-(2-carbethoxycyclohexyl)malonate and MeI], hydrolysed to cyclohexane-1-carboxylic-2- α -propionic acid, m.p. 184°. Attempted methylation (MeI, Na, C_6H_6) gave retrogression products, including $CMe_2(CO_2Et)_2$. Et tiglate (II), b.p. 55–57°/15 mm., and $CHEt(CO_2Et)_2$ also react normally and give 14% of $Et_2 \gamma$ -carbethoxy- $\alpha\beta$ -dimethyl- γ -ethylglutarate, b.p. 151–152°/2.5 mm. [synthesised (b.p. 145–146°/2 mm.) by condensation of (II) with $CHNa(CO_2Et)_2$ to $CO_2Et \cdot CHMe \cdot CH(CO_2Et)_2$, b.p. 147–150°/3 mm., and ethylation], giving on hydrolysis (EtOH–KOH) γ -carboxy- $\alpha\beta$ -dimethyl- γ -ethylglutaric acid, m.p. 158–159°, and on methylation, retrogression products, including (II) and $CMeEt(CO_2Et)_2$. Methylthylmalondianilide has m.p. 174°. $CHMe \cdot C \cdot Et \cdot CO_2Et$ (III), b.p. 62–64°/12 mm., reacts normally with (I) and gives 39% of $Et_2 \alpha$ -carbethoxy- $\alpha\beta$ -dimethyl- γ -ethylglutarate, b.p. 153–155°/3.5 mm. [synthesised (b.p. 154–156°/4 mm.) by condensation of (III) with $CHNa(CO_2Et)_2$ to $Et_2 \alpha$ -carbethoxy- β -methyl- γ -ethylglutarate, b.p. 148–150°/3 mm., and methylation], giving on alkaline hydrolysis, α -carboxy- $\alpha\beta$ -dimethyl- γ -ethylglutaric acid, m.p. 161°, on acid hydrolysis, $\alpha\beta$ -dimethyl- γ -ethylglutaric acid, m.p. 123°, and on methylation, (III) and $CMe_2(CO_2Et)_2$.

Holden and Lapworth's theory of Michael condensations (A., 1931, 1271), viz., reversible isomerisation of the normal product $CHR'X \cdot CR_2 \cdot CR''(CO_2Et)_2$ into the abnormal product $CO_2Et \cdot CR'X \cdot CR_2 \cdot CHR'' \cdot CO_2Et$ via an intermediate cyclic keto-ester, must be assumed valid since it successfully predicts abnormal reactions, and no evidence of Thorpe's mechanism has been found.

Hence (i) additions of $\text{CR}_2\text{CR}'\text{X}$ to malonic esters and their alkyl derivatives will be normal and (ii) additions of CR_2CHX to alkylmalonic esters will be abnormal. The anomalous abnormal addition of alkylmalonic esters to $\text{CR}:\text{C}=\text{CO}_2\text{Et}$ (cf. Farmer, *et al.*, A., 1937, II, 48) is actually normal since these esters may be regarded as α -substituted ethylenic esters. The anomalous normal addition of $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ to $(\text{CH}\cdot\text{COPh})_2$ is due to insolubility of the initial product in the reaction medium, preventing isomerisation. This theory is applicable only to additions in presence of an equiv. of NaOEt , i.e., sufficient to effect isomerisation, and not to those in the presence of small "catalytic" amounts.

E. G. B.

Influence of α -phenyl group in three-carbon tautomerism. I. Tautomerism of α -phenyl- $\alpha\beta$ -, $\beta\gamma$ -unsaturated acids and esters. N. L. PHALNIKAR and K. S. NARGUND (J. Indian Chem. Soc., 1937, 14, 736—747).—The tautomerism of the following systems has been studied [% of $\alpha\beta$ -isomeride at equilibrium, and mobility quoted (cf. Linstead, A., 1927, 1167; Kon *et al.*, A., 1929, 927)]: α -phenylcyclohexylidene- \rightleftharpoons α -phenylcyclohexenyl-acetic acid (42%; 0.00954); α -phenyl- Δ^a - \rightleftharpoons α -phenyl- Δ^b -hexenoic acid (87%; 0.4874); Et α -phenylcyclohexylidene- \rightleftharpoons Et α -phenylcyclohexenyl-acetate (72%; 0.996); Et α -phenyl- Δ^a - \rightleftharpoons Et α -phenyl- Δ^b -hexenoate (94.5; 35.63). The α -Ph group depresses mobility in all cases and, compared with α -Me derivatives, shifts the equilibrium to the $\alpha\beta$ -side in the hexenoic acids and cyclohexenes but not in hexenoic esters. The following are described: α -phenylcyclohexylideneacetic acid, m.p. 134° (Ag salt; Et ester, b.p. 175°/12 mm.; anilide, m.p. 146°; p-toluidide, m.p. 115°); Et α -phenylcyclohexenol-acetate, m.p. 71°; α -phenylcyclohexenylacetic acid, m.p. 107—108° (Ag salt; Et ester, b.p. 170°/12 mm.; anilide, m.p. 168°; p-toluidide, m.p. 174°); α -phenyl- Δ^a -hexenoic acid, m.p. 70—71° (Ag salt; Et ester, b.p. 145—150°/12 mm.; anilide, m.p. 130°; p-toluidide, m.p. 210°); Et β -hydroxy- α -phenylhexoate, b.p. 165°/10 mm.; α -phenyl- Δ^b -hexenoic acid, b.p. 155°/10 mm. (Ag salt; Et ester, b.p. 140°/10 mm.; anilide, m.p. 100°).

F. R. S.

4-Phenylcyclohexylacetic acid. J. W. COOK and F. GOULDEN (J.C.S., 1937, 1559—1560).—Contrary to the claims of Ghosh (cf. Sci. and Cult., 1935, 1, 299; 1937, 3, 55), condensation of Δ^1 -cyclohexenyl-acetic acid with C_6H_6 in presence of AlCl_3 takes place with migration, giving at 0°, room temp., and 100° (bath) 4-phenylcyclohexylacetic acid (I), m.p. 112.5—113.5° (amide, m.p. 195—196°), and a liquid mixture of acids which did not contain the known 2-isomerides. This mixture and (I) are readily sulphonated at 100° with conc. H_2SO_4 . The constitution of (I) is confirmed by dehydrogenation and decarboxylation (Pt-black, 305—310°, in CO_2) to p-methyldiphenyl.

H. G. M.

Unsaturated esters of chaulmoogric acid. K. BURSCHKIES (Ber., 1938, 71, [B], 233—236).—Crotyl, b.p. 168—170°/0.05 mm., oleyl, b.p. 260—270°/0.03 mm., gradually becoming solid when kept at 0°, and cinnamyl, b.p. 210—220°/0.05 mm., chaul-

moograte are obtained by heating the acid chloride with the requisite alcohol in N_2 . Geranyl, b.p. 236—240°/0.1 mm., dl-citronellyl, b.p. 205—210°/0.01 mm., and linaloyl, b.p. 200—210°/0.02 mm., chaulmoograte are obtained from the acid and alcohol at 180°, 130°/12—13 mm., and 180°, respectively. They are better tolerated than the Et or CH_2Ph esters.

H. W.

Nitration of m-methoxycinnamic acid. S. N. CHAKRAVARTI, K. GANAPATI, and S. ARAVAMUDHACHARI (J.C.S., 1938, 171—172).—m-Methoxycinnamic acid and HNO_3 (d 1.48) at 0° yield chiefly 4-nitro-, m.p. 296° (shrinks at 280°) (Me ester, m.p. 163°), 6-nitro-, m.p. 227° (Me ester, m.p. 128°), and 2-nitro-3-methoxycinnamic acid, m.p. 265° (Me ester, m.p. 116°), also being formed. The structures are confirmed by synthesis from the appropriate $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO}$ and $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ -piperidine; 4-nitro-, m.p. 248°, and 6-nitro-3-hydroxycinnamic acid, m.p. 221°, are similarly prepared from $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CHO}$.

J. D. R.

Condensation of aldehydes with acid amides: a variant of Claisen's reaction. G. V. TSCHELINCEV and Z. V. BENEVOLENSKAJA (J. Gen. Chem. Russ., 1937, 7, 2361—2364).— PhCHO , NPh_2Ac , and NaOEt in $\text{EtOH}-\text{C}_6\text{H}_6$ yield NaOBz , $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{Na}$, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NPh}_2$, and NHPh_2 . The diphenylamide, m.p. 186—187°, of furylacrylic acid is obtained similarly from furfuraldehyde.

R. T.

Isomorphism of organic compounds. III. H. LETTRÉ and P. LEHMANN (Ber., 1938, 71, [B], 416—417; cf. A., 1937, II, 339).—The three isomeric iodobenzoic acids do not form mixed crystals with one another, with BzOH , or with the corresponding hydroxy- or methyl-benzoic acids. Such formation is observed with the related chloro- and bromobenzoic acids.

H. W.

Organic reactions with boron fluoride. XVII. Rearrangement of alkyl salicylates and reaction of alcohols with salicylic acid. W. J. CROXALL, F. J. SOWA, and J. A. NIEULAND (J. Org. Chem., 1937, 2, 253—259).— Pr^a , b.p. 236—240°/745 mm., and Pr^b , b.p. 118°/17 mm., salicylate yield identical rearrangement products when treated with BF_3 at 130—140°, viz., 2-hydroxy-3-isopropyl-, m.p. 70—72° (Me ester, b.p. 110°/6 mm.), 2-hydroxy-5-isopropyl-, m.p. 120° (Me ester, b.p. 130°/6 mm.), and 2-hydroxy-3:5-diisopropyl-benzoic acid. Bu^a salicylate, b.p. 146°/20 mm., similarly gives 2-hydroxy-3-sec-butyl- (Me ester, b.p. 116°/5 mm.), 2-hydroxy-5-sec-butyl- (Me ester, b.p. 138°/5 mm.), and 2-hydroxy-3:5-disec-butyl-benzoic acid, whilst Bu^b salicylate, b.p. 135°/17 mm., affords (mainly) 2-hydroxy-5-tert-butylbenzoic acid (Me ester, b.p. 125°/7 mm.). $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is also produced in each rearrangement. Substitution occurs *ortho* and *para* to OH and *meta* to CO_2H . *ortho*-Substitution predominates when Pr^b and sec-Bu groups are introduced whereas Bu^a enters the *para* position almost exclusively. All the isolated products are phenolic, thus showing the absence of any condensation on the OH group as is characteristic in olefine-phenol condensations. The deactivation of the phenolic group affords additional chemical evidence of the

existence of a chelated ring in $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. Since Pr^a , Bu^a , and Bu^b esters rearrange to Pr^b , Bu^b , and Bu^c -substituted acids, respectively, the migration may be considered as taking place through the intermediate olefine stage with subsequent condensation of the activated olefine into an activated position of the aromatic nucleus. The products appear to indicate that the rearrangement is inter- as well as intra-mol. A scheme is suggested. The olefine stage is further verified by rearranging the esters in presence of C_6H_6 or Ph_2O ; most of the alkyl migration takes place to the Ph_2O and the substituent is present as the isomerised alkyl group. $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ reacts with PrOH , BuOH , and BuOH to give the corresponding salicylates in presence of small quantities of BF_3 ; larger quantities result in the production of the same $\text{OH}\cdot\text{C}_6\text{H}_3\text{R}\cdot\text{CO}_2\text{H}$ as are formed by rearrangement of the corresponding esters. It appears that although in the alkylation of phenols the reaction proceeds through the ethers the change in the case of hydroxyaromatic acids occurs through the ester stage. The possibility of direct nuclear condensation of the olefine is not eliminated. AlkOBz do not rearrange to give nuclear-substituted acids, thus showing that OH activates the C_6H_6 nucleus. The following compounds appear new: 2:4-disec.-butylphenol, b.p. 265–267°; 2-, b.p. 285–288°, and 4-, b.p. 302°, -sec.-butyldiphenyl ether. H. W.

Anhydrides of N-arylanthranilic acids. II. J. STEIGMAN and G. POWELL (J. Org. Chem., 1937, 2, 211–212).—N-Arylanthranilic acids are converted into anhydrides (cf. A., 1933, 1291) when treated with $\text{PhSO}_2\text{Cl}\cdot\text{C}_2\text{H}_5\text{N}$. The following anhydrides are described: N-o-ethoxyphenylanthranilic (I), m.p. 135–137°; N-o-chlorophenylanthranilic (II), m.p. near 170°; N-o-tolylanthranilic (III), m.p. 164–166°; NN-di-o-tolylanthranilic, m.p. 188–191°; N-mesitylanthranilic, m.p. 200–203°. When heated with $\text{AcOH}\cdot\text{NaOAc}$ or dil. alkalis in EtOH rearrangement to compounds of a peptide type occurs if a H is still available on the N for rearrangement. The compound from (I) has m.p. 188–190°, and is sol. in dil. aq. NH_3 , and that from (II), m.p. near 225° (decomp.), but that from (III), variable m.p., was probably not obtained pure. H. G. M.

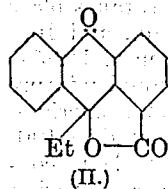
Dissociable anthracene oxides. Derivatives of 9:10-diphenylanthracene. L. VELLUZ and (MMR.) VELLUZ (Bull. Soc. chim., 1938, [v], 5, 192–196; cf. A., 1937, II, 374).—2-Substitution by Br, CO_2H , or CO_2Me has no appreciable effect on the reversible photo-oxidisability of 9:10-diphenylanthracene. 2-Bromo-9:10-dihydroxy-9:10-diphenylanthracene, m.p. 210° (all m.p. are on block) (from MgPhBr and 2-bromoanthraquinone), with $\text{AcOH}\cdot\text{KI}$ gives 2-bromo-9:10-diphenylanthracene (I), m.p. 186°, solar irradiation of which in CS_2 (1 hr.) yields a photo-oxide, decomp. about 180°. 9:10-Diphenylanthracene-2-carboxylic acid (II), m.p. 294° [from Mg derivative of (I) and CO_2], gives a fluorescent CS_2 solution, yielding after 2 hr. solar irradiation a photo-oxide, decomp. about 180°. Me 9:10-diphenylanthracene-2-carboxylate (III), m.p. 170° [from (II) and CH_2N_2], gives a photo-oxide, m.p. about 220° (decomp.), also obtained from the photo-oxide of (II) and CH_2N_2 .

Thermal decomp. of the oxides in a vac. yields O_2 and the original anthracene. E. G. B.

Electrolysis of aromatic carboxylic acids. VI. Opianic acid. V. M. RODIONOV and V. K. ZVORYKINA (J. Gen. Chem. Russ., 1937, 7, 2633–2636).—Meconine formed during electrolysis of opianic acid (A., 1936, 1516) does not originate from reduction of α - and β -dimeconyl formed simultaneously, as these are reduced electrolytically, or with $\text{Na}\cdot\text{Hg}$, to α -veratrylmeconine-2'-carboxylic acid, m.p. 177–178°. R. T.

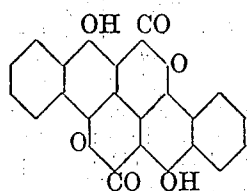
Reaction between maleic anhydride and polycyclic hydrocarbons. W. E. BACHMANN and M. C. KLOETZEL (J. Amer. Chem. Soc., 1938, 60, 481–485).—Addition of maleic anhydride (1 mol.) to anthracene derivatives (1 mol.) in boiling xylene is reversible, giving the following amounts of adduct at equilibrium: anthracene 99, 9-methyl- 99, 9:10-dimethyl- (I) 98, 9-phenyl- (II) 75, 9:10-diphenyl- (III) 16, 1:2-benz- (IV) 84, and 1:2:5:6-dibenzanthracene (V) 30, 3-methylcholanthrene (VI) 22%. Use of 30 mols. of anhydride increases the yields to (II) 97, (III) 78, (IV) 99, (V) 91, and (VI) 83%. Lower temp. favours addition, a 1:1 mixture of anhydride and (VI) giving 94% of adduct in boiling C_6H_6 , whereas the adducts from (IV) and (II) do not dissociate therein. *meso*-Me accelerates, but *meso*-Ph greatly and 1:2- or 5:6-benz- markedly reduces, the rate of condensation. (I) reacts rapidly at room temp. in C_6H_6 , but 1:1 mixtures of anhydride with (II) or (III) react only slowly in boiling C_6H_6 . 9-Methyl-, m.p. 264–266°, 9:10-dimethyl-, m.p. 333–335° [the corresponding acid readily gives the anhydride in hot EtOAc], and 9:10-diphenyl-anthracene-9:10-endo- $\alpha\beta$ -succinic anhydride, m.p. 249–250° (decomp.), 3-methylcholanthrene-6:12b-endo- $\alpha\beta$ -succinic anhydride, m.p. 209–210° (decomp.) (the acid is dehydrated in hot EtOAc , but with $\text{CH}_2\text{N}_2\cdot\text{aq. COMe}_2$ gives the Me_2 ester, m.p. 165.5–166.5°), and Me_2 1:2:5:6-dibenzanthracene-9:10-endo- $\alpha\beta$ -succinate, m.p. 230–231°, are described. R. S. C.

Cyanoanthracenes. I. H. WALDMANN and A. OBLATH (Ber., 1938, 71, [B], 366–370).—Anthracene-1-carboxylamide with boiling $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ gives 1-cyanoanthracene (I), m.p. 144.5°, oxidised by CrO_3 in AcOH to 1-cyanoanthraquinone. MgEtI in Et_2O converts (I) into 1-propionylantracene, m.p. 52° (semicarbazone, m.p. 209°), also obtained with some difficulty from anthracene-1-carboxyl chloride and ZnEtI . Anthraquinone-1-carboxyl chloride and ZnEtI afford 9-hydroxy-9-ethyl-10-anthrone-1-carboxylactone (II), m.p. 153°. 1-Propionylantracene, m.p. 164.5°, is converted by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in boiling PhMe into the diazine, $\text{C}_{17}\text{H}_{12}\text{ON}_2$, m.p. 204°. 1-Benzoylanthracene, m.p. 141°, from (I) and MgPhBr in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$ is oxidised to 1-benzoylanthraquinone, m.p. 229°. 1-o-Toluyol-, m.p. 104°, and 1- α -naphthoyl-, m.p. 160.5°, -anthracene are described. Similarly anthracene-1:4-dicarboxylamide is transformed into 1:4-dicyanoanthracene, m.p. 268.5°. 2-Cyanoanthracene, m.p. 200°, gives 2-benzoylanthracene, m.p. 175° and, after re-solidification, m.p.



187°; oxidised to 2-benzoylanthraquinone, m.p. 213°. 1:8-Dichloroanthraquinone, CuCN, and $\text{CH}_2\text{Ph}\cdot\text{CN}$ at 230° give 1:8-dicyanoanthraquinone, m.p. >390°. This is hydrolysed by $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ at 170° to anthraquinone-1:8-dicarboxylic acid, m.p. 316°, which is reduced by Zn dust and NH_3 to anthracene-1:8-dicarboxylic acid, decomp. 345°. H. W.

Constitution of Russig's compound (supposed 6:13-dihydroxypentacene-5:14-7:12-diquinone). C. MARSCHALK (Bull. Soc. chim., 1938, [v], 5, 156—164; cf. A., 1929, 1436, 1453; 1930, 608, 1187; 1936, 1513).—Russig's compound (I) (A., 1900, i, 601) and Zn dust at 500—550° in H_2 give a hydrocarbon, m.p. 310°, oxidised to a compound, m.p. 205—206°, unlike any known pentacenequinone. 5:7:12:14-Tetrahydroxypentacene-6:13-quinone similarly gives 6:13-dihydropentacene, m.p. 271—



(A.)

272°, oxidised to pentacene-6:13-quinone. (I) is therefore not a pentacene derivative but is formed from 1:4-dihydroxynaphthalene-2-carboxylic acid by a condensation analogous to that of gallic to ellagic acid; structure (A) is assigned to (I) and is confirmed by scission with KOH at 250—260° to 1:4:1':4'-tetrahydroxy-2:2'-dinaphthyl, oxidised to 2:2'-dinaphthyl-1:4:1':4'-diquinone (synthesis from Na salt of 4-benzeneazo- α -naphthol and FeCl_3 described), and acetylated to the Ac_4 derivative, also obtained from the diquinone, NaOAc , Ac_2O , and Zn dust. E. G. B.

Choladienic acid. S. MIYAZI (J. Biochem. Japan, 1937, 26, 333—336).—Vac. distillation of chenodeoxycholic acid and repeated crystallisation of the product from EtOH affords choladienic acid (I), m.p. 147—148°, $[\alpha]_D^{25} -43.59^\circ$ in CHCl_3 (probably identical with ursocoladienic acid of Iwasaki, A., 1937, II, 20). The Et ester, m.p. 75°, $[\alpha]_D^{25} -50.24^\circ$ in CHCl_3 , is hydrolysed to (I), m.p. 150°, from which were prepared the tetrabromide, m.p. 186—187° (decomp.), and, by dissolving in AcOH and hydrogenating, cholanolic acid. F. O. H.

Derivatives of cis-3-hydroxy- Δ^5 -cholenic acid. G. A. D. HASLEWOOD (J.C.S., 1938, 224—228).—Me cis-3-acetoxy- Δ^5 -cholenate, oxidised (CrO_3 in AcOH) yields Me cis-7-keto-3-acetoxy- Δ^5 -cholenate (I), m.p. 177—178° [hydrolysed (NaOH) to cis-3-hydroxy-7-keto- Δ^5 -cholenic acid, m.p. 223—225°, $[\alpha]_D^{25} -115^\circ$ in EtOH (semicarbazone, decomp. 267—269°)], and Me 6-keto-3:5-diacetoxycholanate, m.p. 172—173°, hydrolysed (NaOH) to 3:5-dihydroxy-6-ketocholanolic acid, m.p. 278—279°, $[\alpha]_D^{25} -38^\circ$ in EtOH (semicarbazone, decomp. 267—269°), which, treated successively with CH_2N_2 and Ac_2O , yields Me 5-hydroxy-6-keto-3-acetoxycholanate, m.p. 203—204°. (I) with $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH and then with KOH-MeOH yields Me 3:7-dihydroxy- Δ^5 -cholenate, m.p. 142—144° [dibenzoate (II), m.p. 165—166° (by $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}$), hydrolysed to 3:7-dihydroxy- Δ^5 -cholenic acid (III), m.p. 188—190° (decomp.), $[\alpha]_D^{25} -54^\circ$ in EtOH]. When refluxed with NPhMe_3 , followed by hydrolysis of the product with NaOH, (II) yields

cis-3-hydroxy- Δ^5 -7-choladienic acid (IV), m.p. 214—216° (decomp.), $[\alpha]_D^{25} -69^\circ$ in EtOH, converted by successive treatment with CH_2N_2 and $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ into Me cis-3-acetoxy- Δ^5 -7-choladienate, m.p. 125—127°. Pyrolysis of (II) at 195—200°/0.1 mm. yields a substance, m.p. 165—166° (hydrolysed to an acid, $\text{C}_{24}\text{H}_{38}\text{O}_4$, m.p. 214—216°), (III), and a little (IV). J. D. R.

Aldehydes and hydroxyaldehydes of the polymethylene series. VI. Rearrangements of α -hydroxyhexahydrobenzaldehyde. E. D. VENUS-DANILOVA and V. F. KAZIMIROVA (J. Gen. Chem. Russ., 1937, 7, 2639—2648).—1-Hydroxycyclohexanecarbaldehyde (I) in EtOH or MeOH and 1% H_2SO_4 (8 hr. at 145°) yields 2-ethoxy-, b.p. 78—79°/16 mm., or 2-methoxy-suberone. In absence of alcohols the product is 2-hydroxysuberone (II). (I) and aq. KOH at 100° in presence of PbO yield (II), together with 1-hydroxymethylcyclohexanol, cyclohexanecarboxylic acid, and 1-hydroxycyclohexanecarboxylic acid. R. T.

Synthesis of terephthal- and isophthalaldehydic esters. K. H. SLOTTA and R. KETHUR (Ber., 1938, 71, [B], 335—341).— $m\text{-CN}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ is scarcely affected by prolonged boiling with conc. HCl and is stable towards 80% H_2SO_4 . $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ suspended in a mixture of EtOH, AcOH, conc. HCl, and dil. $\text{Pb}(\text{OAc})_2$ is reduced at a Pb foil cathode, the anode being a Pb rod in 10% H_2SO_4 ; the Et and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl}$ esters are similarly reduced to the NH_2 -ester and the process is applicable to the corresponding esters of $m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. β -Chloroethyl m -aminobenzoate has m.p. 54°. The NH_2 -compounds are converted (Sandmeyer) into the CN-derivatives; Et, b.p. 152°/14 mm., m.p. 50°, and β -chloroethyl, b.p. 210—215°/14 mm., m.p. 89—90°, p -cyanobenzoate and β -chloroethyl m -cyanobenzoate, b.p. 198—200°/13 mm., m.p. 60°, obtained from m -cyanobenzoyl chloride, b.p. 145°/? pressure (from the acid and boiling SOCl_2), and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$, appear new. For the transformation of $\cdot\text{CN}$ into $\cdot\text{CHO}$ the method followed is essentially that of Stephen (A., 1925, i, 1131). The SnCl_4 used should not be quite anhyd. and is best obtained by dehydrating cryst. SnCl_4 over conc. H_2SO_4 at room temp. and adding thereto about 10% of its wt. of the crystals. Thus addition of $p\text{-CN}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ to this material in Et_2O saturated with HCl followed by hydrolysis of the aldimine gives Me terephthalaldehyde, b.p. 135°/12 mm., m.p. 60° in 90% yield. Terephthalaldehydic acid, its chloride, b.p. 163—165°/18 mm., its Et, b.p. 142°/13 mm., and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot$, b.p. 206—207°/12 mm., ester are described. The Me, Et, and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot$ esters of isophthalaldehydic acid have b.p. 152—153°/15 mm. (m.p. 58°), 162—164°/13 mm., and 209—211°/12 mm., respectively. H. W.

Products of the diene synthesis with piperylene and hexadiene. B. ARBUSOV, Z. ZINOVIEVA, and I. FINK (J. Gen. Chem. Russ., 1937, 7, 2278—2291).— $\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ or $\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}$ and $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$ or $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ at 120° (5 hr.) yield 5-methyl- (I), 2:5-dimethyl- (II), or 2:5:6-trimethyl- Δ^3 -cyclohexen-1-al (III), which condense with ketones to yield the following: β -2:5-dimethyl- Δ^3 -

cyclohexenylvinyl Et, b.p. 132—135°/10 mm., Pr^a , b.p. 154—155°/10 mm., and isobutenyl ketone, b.p. 138—140°/9 mm.; β -5-methyl- Δ^3 -cyclohexenylvinyl Et ketone, b.p. 140°/22 mm. With EtCHO, (I) and (II) are said to give 5-methyl-, b.p. 110—112°/20 mm., and 2:5-dimethyl-1:2:5:6-tetrahydrostyrylacetaldehyde, b.p. 120—121°/10 mm., respectively. (I) and $CHNaAc \cdot CO_2Et$ lead to Et 3-methyl-1:2:3:6-tetrahydrocinnamate, b.p. 124—125°/12 mm. The Et, b.p. 117—119°/11 mm., and Bu^a , b.p. 153—155°/9 mm., acetals of (II), and the Et acetal of (I), b.p. 91—93°/10 mm., are described. The following alcohols were obtained (Grignard reaction) from (II) or (III): 2:5-dimethyl- Δ^3 -cyclohexenyl-ethyl-, (IV), b.p. 120—123°/28 mm., -n-propyl-, b.p. 120—122°/10 mm., -isobutyl-, b.p. 124—126°/10 mm., and -phenyl-carbinol, b.p. 167—168°/9 mm., and 2:5:6-trimethyl- Δ^3 -cyclohexenyl-ethyl-, b.p. 116—118°/15 mm., -n-propyl-, b.p. 118—120°/12 mm., and -isobutyl-carbinol, b.p. 132—134°/30 mm. (IV) and CrO_3 in aq. H_2SO_4 yield 2:5-dimethyl- Δ^3 -cyclohexenyl Et ketone, b.p. 100—102°/12 mm. (semicarbazone, m.p. 160°) R. T.

Synthesis of cyclopentenones. I. J. RINKES (Rec. trav. chim., 1938, 57, 176—178; cf. Plattner and Pfau, A., 1938, II, 15).—1-Methylcyclopentanol [from cyclopentanone (I) and $MgMeI$] is dehydrated ($KHSO_4$) to 1-methyl- Δ^1 -cyclopentene, the nitroschloride, m.p. 76°, of which is converted by successive treatment with $AcOH \cdot NaOAc$ and dil. H_2SO_4 into 2-methyl- Δ^2 -cyclopentenone. 2-n-Amyl- Δ^2 -cyclopentenone is similarly prepared starting with (I) and Mg n-amyl bromide. R. G.

Molecular rearrangements in dehydration of active and inactive 3-methyl-1- α -hydroxyisopropylcyclohexanols. M. GODCHOT and G. CAUQUIL (Compt. rend., 1938, 206, 297—299).—Dehydration of the glycols (A., 1938, II, 96) affords a mixture of three ketones: cis-3-acetyl-1:3-dimethylcyclohexane [dl-, b.p. 94.5°/15 mm. (oxime, m.p. 58°, b.p. 140°/14 mm.; semicarbazone, m.p. 174°), and d-, b.p. 92°/15 mm., $[\alpha]_{5461} +11.85^\circ$ (oxime, m.p. 59°, b.p. 140°/15 mm.; semicarbazone, m.p. 189°), -forms]; cis-trans-3-acetyl-1:3-dimethylcyclohexane [dl-, b.p. 84°/15 mm. (oxime, b.p. 138°/14 mm.), and l-, b.p. 86°/14 mm., $[\alpha]_{5461} -13.15^\circ$ (oxime, b.p. 140°/15 mm.), -forms]; 2:2:4- (or 2:2:6-)trimethylcycloheptanone [dl-, b.p. 85°/14 mm. (semicarbazone, m.p. 153°), and l-, b.p. 84°/14 mm., $[\alpha]_{5461} -22.7^\circ$ (semicarbazone, m.p. 152°), -forms]. The 3-acetyl-1:3-dimethylcyclohexanes with $NaOBr$ give $CHBr_3$ and respectively dl-cis-, m.p. 44°, b.p. 140°/13 mm. (amide, m.p. 84.5°), active cis-, m.p. 53°, b.p. 135°/14 mm. (amide, m.p. 48.5°), dl-cis-trans-, m.p. 90° (chloride, b.p. 98°/14 mm.; amide, m.p. 73°), and active trans-, b.p. 135°/15 mm. (chloride, b.p. 99°/14 mm.), -1:3-dimethylcyclohexane-3-carboxylic acids. E. G. B.

Constitution of the methylionones. G. W. POPE and M. T. BOGERT (J. Org. Chem., 1937, 2, 276—287).— $m\text{-}C_6H_4EtBr$, b.p. 92°/24 mm., obtained from $m\text{-}C_6H_4Ac \cdot NH_2$, is converted by Mg followed by $(CH_3)_2O$ into β -m-ethylphenylethanol, b.p. 110—111°/4 mm. (phenylurethane, m.p. 57.5—58°; 3:5-dinitrobenzoate, m.p. 79—79.5°), whence by $HBr + H_2SO_4$ or PBr_3 β -m-ethylphenylethyl bromide, b.p. 105—106°/

6 mm., which with Mg followed by Pr^aCHO affords ε -m-ethylphenyl- β -methylpentan- γ -ol (I), b.p. 132—133°/4 mm., which does not give a cryst. phenylurethane or 3:5-dinitrobenzoate. When heated with P_2O_5 (I) yields 1:1-dimethyl-6-ethyl-1:2:3:4-tetrahydronaphthalene (II), b.p. 104—105°/4 mm. [$(NO_2)_2$ -derivative, m.p. 111—112°; corresponding sulphonamide, m.p. 129—130°], oxidised by alkaline $KMnO_4$, dil. HNO_3 , or $Na_2Cr_2O_7 + H_2SO_4$ to α -2:4-dicarboxyphenylisobutyric acid, which softens with loss of H_2O at 160° and passes into the anhydride, m.p. 214—215°. Dehydrogenation of (II) by Se at 300—320° gives 1:6- $C_{10}H_6MeEt$, b.p. 146°/14 mm. (picrate, m.p. 80—81°; styphnate, m.p. 88.5—89.5°). 1:2:4- $C_6H_3Me_2Br$ is transformed by Mg and $(CH_3)_2O$ into β -o-4-xylylethanol (III), b.p. 109—110°/3 mm. (phenylurethane, m.p. 108—108.5°; 3:5-dinitrobenzoate, m.p. 145—146°), and 3:4:3':4'-tetramethyldi-phenyl, m.p. 76—77°. (III) with conc. H_2SO_4 and 48% HBr yields β -o-4-xylylethyl bromide, b.p. 106—107°/4 mm., whence ε -o-4-xylyl- β -methylpentan- γ -ol, b.p. 127—128°/3 mm., which does not yield a cryst. phenylurethane or 3:5-dinitrobenzoate. It is cyclised by P_2O_5 (yield 90%) to 1:1:6:7-tetramethyl-1:2:3:4-tetrahydronaphthalene (IV), b.p. 103—104°/4 mm. (corresponding sulphonamide, m.p. 137—138°). (IV) with alkaline $KMnO_4$ gives α -2:4:5-tricarboxyphenylisobutyric acid, m.p. 267—269° (sealed tube), which gives the anhydrides, $(CO_2H)_2C_6H_2 \begin{smallmatrix} CO-O \\ \diagup \quad \diagdown \\ CMe_2 \end{smallmatrix} CO$ and $O \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CMe_2 \end{smallmatrix} C_6H_2 \begin{smallmatrix} CO-O \\ \diagup \quad \diagdown \\ CMe_2 \end{smallmatrix} O$ when heated in an open tube. (IV) is dehydrogenated by Se at 300—320° to 2:3:5- $C_{10}H_5Me_3$. Methyl- ψ -ionone, obtained from citral (V) and $COMeEt$, is cyclised to " α -methylionone" by 85% H_3PO_4 . This is dehydrated by distillation with 1% of I to (II), showing that condensation of (V) has occurred essentially if not exclusively with $\cdot COMe$ and not with Et . Five technical samples of " α -methylionone" give similar results. M.p. are corr. H. W.

Action of mixed organomagnesium derivatives on dimethylbutylacetophenone [phenyl α -dimethylamyl ketone]semicarbazone. (MLLE.) D. BICQUARD (Bull. Soc. chim., 1938, [v], 5, 207—215; cf. A., 1936, 725, 739).—The apparent absence of a double linking between the aromatic and functional groups in dimethylbutylacetophenonesemicarbazone (I), indicated by the absorption, is attributed either to deformation of the valency angle in the structure $CMe_2Bu \cdot CPh \cdot N \cdot NH \cdot CO \cdot NH_2$ or to possession of a cyclic structure $CMe_2Bu \cdot CPh \begin{smallmatrix} NH \\ \diagup \quad \diagdown \\ N \cdot CO \cdot NH_2 \end{smallmatrix}$ or

$CMe_2Bu \cdot CPh \begin{smallmatrix} NH \cdot NH \\ \diagup \quad \diagdown \\ NH \cdot CO \end{smallmatrix}$ (I) contains 3 active H and with $MgEtBr$ in Et_2O and C_6H_6 yields (after treatment with aq. HCl) a mixture from which have been isolated $COPhEt$, a compound, $(C_{15}H_{25}N_4Cl)_3$, m.p. 217° [giving with $NaOH$ a compound, $(C_{14}H_{25}N)_4$ (II), m.p. 130°], and $\delta\delta$ -dimethyloctan- γ -one (40% yield) (semicarbazone, m.p. 133°); C_6H_6 is isolable using Et_2O -isoamyl ether as solvent. In Et_2O alone, (I) and $MgEtBr$ yield a compound, b.p. 165°/0.2 mm., m.p. 43°, probably $CMe_2Bu \cdot CPh_2 \cdot NH \cdot NH \cdot CN$ (converted by Ac_2O into a compound, $C_{11}H_{21}O_5N_2$, m.p. 89°),

and a compound, $C_{24}H_{35}N_3$, b.p. $195^\circ/0.2$ mm., m.p. 82° . With $MgBuCl$, (I) gives $COPhBu$, $BuCO\cdot NH_2$, and a compound, $C_{32}H_{53}O_2N_3Cl_2$, m.p. $170-180^\circ$ [giving (II) with $NaOH$]; ζ -dimethyldecan- ϵ -one is not produced. The following mechanism is proposed: (I) with $MgRX$ gives $CMe_2Bu\cdot CPhR\cdot N(MgX)\cdot N(MgX)\cdot CO\cdot N(MgX)_2$, decomp. into either $MgPhX$ and $CMe_2Bu\cdot CR\cdot N\cdot N(MgX)\cdot CO\cdot N(MgX)_2$ (III) or $CMe_2Bu\cdot MgX$ and $CPhR\cdot N\cdot N(MgX)\cdot CO\cdot N(MgX)_2$ (IV). With excess of $MgRX$, (III) gives $CMe_2Bu\cdot CR\cdot NMgX$, $NR(MgX)_2$, and $COR\cdot N(MgX)_2$, whilst (IV) gives $CPhR\cdot NMgX$, $NR(MgX)_2$, and $COR\cdot N(MgX)_2$. Hydrolysis thus gives finally C_6H_6 , $CMc_2Bu\cdot COR$, NH_2R , $COR\cdot NH_2$, $CHMe_2Bu$, and $COPhR$. These and earlier results show that $MgRX$ adds to the $C\cdot N$ of semicarbazones in which this double linking cannot migrate. E. G. B.

5-Aldehydoacetovanillone, a substance closely resembling picric acid in its strongly acidic nature. S. KAWAI, F. YOSHIMURA, and K. ASHINO [with T. NAKAMURA] (Ber., 1938, 71, [B], 324—328).—Acetovanillone (I), $CH_2\cdot CH\cdot CH_2Br$, and anhyd. K_2CO_3 in boiling $COMe_2$ yield acetovanillone allyl ether, b.p. $153^\circ/5$ mm., m.p. $41-42^\circ$, isomerised at about 230° to 5-allylacetovanillone, b.p. $155-161^\circ/5$ mm., m.p. $79-80^\circ$. This is converted by KOH in boiling amyl alcohol containing a little H_2O into 5-propenylacetovanillone, m.p. $67-68^\circ$, which is ozonised in $EtOAc$ at 0° and then hydrogenated (Pt-black) to 5-aldehydoacetovanillone (II), m.p. $145-146^\circ$ (monoxime, m.p. 215°), with a small proportion of 5-propylacetovanillone, m.p. $98-99^\circ$. In qual. colour reactions (II) closely resembles $o\text{-OH}\cdot C_6H_4\cdot CHO$; it is immediately sol. in aq. $NaHCO_3$ to a lemon-yellow solution. Oxidation of the condensation product from (I) and $NPh\cdot CH_2$ by $PhNO_2\text{-}NaOH$ gives 2:2'-dihydroxy-3:3'-dimethoxy-5:5'-diacetyldiphenylmethane, m.p. 226° . H. W.

Condensations brought about by bases. II. Condensation of the enolate of ethyl isobutyrate with ethyl benzoate. Claisen type of condensation. W. B. RENFREW, jun., and C. R. HAUSER (J. Amer. Chem. Soc., 1938, 60, 463—465; cf. A., 1937, II, 482).—The Claisen condensation may occur even if the β -keto-ester produced cannot enolise, for Pr^aCO_2Et and $EtOBz$ in presence of CPh_3Na give $COPh\cdot CMe_2\cdot CO_2Et$. This product dissociates, for, if the reaction mixture is kept for several days, only $EtOBz$ and $COPr^a\cdot CMe_2\cdot CO_2Et$ are obtained. During Claisen condensations a strong base is replaced by a weaker one, but the possibility of this occurring is alone not enough to initiate reaction. R. S. C.

α - and β -Naphthoylacetic esters. A. WAHL, M. GOEDKOOP, and E. HEBERLEIN (Compt. rend., 1938, 206, 191—193).—*Et* α -naphthoyl-, an oil, decomp. on heating (*Cu* salt, m.p. 196°), and β -naphthoyl- (*Cu* salt, m.p. 203.5°) -acetates are prepared from the *Et* naphthoate (1 mol.), Na (3 atoms), and $EtOAc$ (excess). The following derivatives are described: 3- α -, m.p. 233° , and - β -, m.p. 190° , naphthyl-, 1-phenyl-3- α -, m.p. 199° , and - β -, m.p. 127.5° , and 1-*p*-nitrophenyl-3- α -, m.p. 228° , and - β -, m.p. 235° , -naphthyl-5-pyrazolones; *Et* oximino- α -, m.p. 135.5° , and - β -,

m.p. 153° (acid, m.p. 140°), -naphthoylacetic; β -naphthylisooxazolone, m.p. 159° ; β -naphthoylacetic anilide, m.p. $130-131^\circ$. E. G. B.

Methyl 3-methoxy-2-naphthoylacetic. H. WAHL (Compt. rend., 1938, 206, 521—523; cf. preceding abstract).—*Me* 3-methoxy-2-naphthoate with $MeOAc$ and Na in $PhMe$ at 100° affords 3-methoxy-2-naphthoic acid and *Me* 3-methoxy-2-naphthoylacetic (I), b.p. $200^\circ/2$ mm. (slight decomp.), m.p. 57° (*Cu* derivative, m.p. 215°), which with $NH_2OH\cdot HCl$, $N_2H_4\cdot H_2O$, $NHPh\cdot NH_2$, and $NO_2\cdot C_6H_4\cdot NH\cdot NH_2$ in $AcOH\text{-}EtOH$ gives 3-(3'-methoxy-2'-naphthyl)-5-isooxazolone, m.p. 149.5° , -5-pyrazolone, m.p. 205° , -1-phenyl-5-pyrazolone, m.p. 175° , and -1-*p*-nitrophenyl-5-pyrazolone, m.p. 235° , respectively. (I) with amyl nitrite in $AcOH$ gives *Me* α -oximino- α -3-methoxy-2-naphthoylacetic, m.p. 131° , and with $p\text{-NO}_2\cdot C_6H_4\cdot N_2Cl$ gives *Me* α -*p*-nitrobenzeneazo- α -3-methoxy-2-naphthoylacetic, m.p. 213° . Prolonged boiling of (I) with 20% H_2SO_4 affords some *Me* 3-hydroxy- β -naphthyl and 3-methoxy- β -naphthyl ketone (semicarbazone, m.p. $238-240^\circ$; oxime, m.p. 121.5° ; phenylhydrazone, m.p. 146° ; *p*-nitrophenylhydrazone, m.p. 226°). J. L. D.

Aroylacetonitriles.—See B., 1938, 322.

Bisphenylpyruvic acid. J. JARROUSSE (Ann. Chim., 1938, [xi], 9, 157—232).—A résumé and extension of work previously abstracted (A., 1935, 488; 1936, 73, 1252; 1937, II, 150). Reasons are advanced in favour of the view that bisphenylpyruvic acid (I), previously regarded as α -hydroxy- γ -keto- β -phenyl- α -benzylglutaric acid, should be considered as α -keto- γ -carboxy- $\beta\delta$ -diphenyl- γ -valerolactone with a very mobile lactone group. Reduction of (I) by $Na\text{-}Hg$ in acid solution gives α -hydroxy- γ -carboxy- $\beta\delta$ -diphenyl- γ -valerolactone (II), m.p. 225° , hydrated by alkalis to $\alpha\gamma$ -dihydroxy- β -phenyl- γ -benzylglutaric acid, m.p. about 140° (*K* salt; *Me* ester, m.p. $131-132^\circ$), which loses H_2O at its m.p. giving a lactone, m.p. 136° , either $CH_2Ph\cdot C(OH)(CO_2H)\cdot CO$ or a stereoisomeride of (II). Very cautious oxidation of (I) by $KMnO_4$ permits the isolation of benzoylbenzylglycollic acid, decomp. $<100^\circ$, transformed by alkali into $OH\cdot CHPh\cdot CO\cdot CH_2Ph$ (III). Similarly oxidation of α -keto- $\beta\delta$ -diphenyl- γ -valerolactone, α -keto- $\beta\gamma$ -diphenyl- γ -butyrolactone, and α -keto- β -phenyl- γ -butyrolactone affords $H_2C_2O_4$ and $OH\cdot CHBz\cdot CH_2Ph$ [converted by alkali into (III)], benzoin, and $CH_2Bz\cdot OH$, respectively, so that the reaction is general in character. Me_2SO_4 and alkali convert (I) into the *Me* ether *Me* ester, $CH_2Ph\cdot C(CO_2Me)(CO_2Me)\cdot O$, m.p. 84° (block). Similarly $CH_2Ph\cdot CO\cdot CO_2H$ affords α -methoxycinnamic acid, m.p. 128° , and benzylpyruvic acid gives (?) α -methoxy- γ -phenyl- Δ^a -butenoic acid, m.p. $36-37^\circ$. H. W.

Condensation products of indan-1-one with nitroso-compounds and aldehydes. P. FRIEGER and E. MILZ (Ber., 1938, 71, [B], 272—279; cf. A., 1935, 1369).—Indan-1-one (I), m.p. 42° , obtained by cyclisation of $CH_2Ph\cdot CH_2\cdot COCl$ by $AlCl_3$, is converted by $PhNO$ and $KOH\text{-}MeOH$ at room temp. into

indanetrione-2:3-dianil N-monoxide,

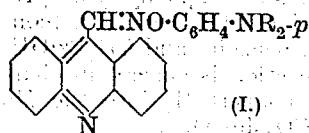
$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(NPh:O)} \\ \text{CO} \end{smallmatrix} \text{C:NPh}$, m.p. 165°, transformed by $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in EtOH-AcOH into 1:2-*indenophenazinone-3-anil N-oxide*, m.p. 222–223°, and thence by AcOH-H₂SO₄ into 1:2-*indophenazin-3-one*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO:C:N} \\ \text{C:N} \end{smallmatrix} \text{C}_6\text{H}_4$ (II), m.p. 219°, identical

with the substance obtained by Ruhemann (J.C.S., 1910, 97, 1449) from triketoindane and $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$. Similarly (I) and $p\text{-NO-C}_6\text{H}_4\text{NMe}_2$ afford *indanetrione-2:3-di-p-dimethylaminoanil N-oxide*, m.p. 180° (with small amounts of a *by-product*, $\text{C}_{34}\text{H}_{30}\text{O}_3\text{N}_4$, m.p. 283–285°), converted by $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ into 1:2-*indenophenazinone-3-p-dimethylaminoanil N-oxide*, $p\text{-NO-C}_6\text{H}_4\text{OMe}$ does not appear to give simple condensation products, those isolated being a *substance*, $\text{C}_{32}\text{H}_{24}\text{O}_5\text{N}_2$, m.p. 292–293°, 4:4'-dimethoxyazobenzene, and 4:4'-dimethoxyazoxybenzene. Condensation of (I) with ArCHO occurs normally, thus giving 2-benzylidene-, m.p. 110–111°, 2-*o-anisylidene*-, m.p. 133° (*perchlorate*, m.p. about 200–205° after softening), 2-*m-anisylidene*-, m.p. 142° (*perchlorate*, m.p. about 190–195° after softening), and 2-*p-anisylidene*-, m.p. 141° (*perchlorate*, m.p. 206–209° after softening), *indanone*. 2-*p-Dimethylamino-benzylideneindanone*, m.p. 165°, yields a colourless

perchlorate, $[\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{C:CH-C}_6\text{H}_4\text{NMe}_2\text{H}](\text{ClO}_4)$, with HClO₄ in AcOH if the solution is cooled slowly, but a violet *perchlorate*,

$[\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{C(OH)} \end{smallmatrix} \text{C:CH-C}_6\text{H}_4\text{NMe}_2](\text{ClO}_4)$, if separation occurs from the hot solution. H. W.

Reactive methylene groups and nitroso-compounds. E. BERGMANN (J.C.S., 1937, 1628).—Fluorene when boiled (4 hr.) with $p\text{-NO-C}_6\text{H}_4\text{NMe}_2$ in EtOH-NaOEt yields *p-dimethylaminophenyldiphenylenemethylenenitrone* (cf. lit.) but no anil, and similarly 2:7-dibromofluorene gives *p-dimethylaminophenyl-2':7'-dibromodiphenylenemethylenenitrone*, m.p. 224° (decomp.). Considerable quantities of azoxydimethylaniline are also formed. The mechanism of nitrene formation of Schönberg *et al.* (A., 1937, II, 248) accounts for the formation from 5-methylacridine and $p\text{-NO-C}_6\text{H}_4\text{NAlk}_2$ of deeply coloured products (cf. A., 1912, i, 655), which should be formulated as (I). The



mechanism is used to explain the reaction of safrole with PhNO and the resistance to such reaction of *isosafole*. Fluorenone with $p\text{-NH}_2\text{-C}_6\text{H}_4\text{NMe}_2$ and a little HCl gives *fluorenone-p-dimethylaminoanil*, m.p. 100°.

H. G. M.

Synthesis of substances related to the sterols. XIX. R. ROBINSON and J. WALKER (J.C.S., 1938, 183–188)—1-Keto-7-methoxy-1:2:3:4:9:10:11:12-octahydrophenanthrene-*b* (I) (improved prep.) and Et₂C₂O₄ in Et₂O with EtOH-free NaOEt yield the enolic *lactone*, m.p. 184–186° (decomp.), of 1-keto-7-methoxy-1:2:3:4:9:10:11:12-octahydro-2-phen-

anthroylformic acid (II), whilst in C₆H₆, the *Et* ester (III), m.p. 98–99° (decomp. > ca. 138°), of (II) is formed. (III) heated to 170° loses CO and yields Et 1-keto-7-methoxy-1:2:3:4:9:10:11:12-octahydrophenanthrene-2-carboxylate, b.p. ca. 205°/0.5 mm., methylated (K-MeI in C₆H₆) to the 2-Me derivative, which with Zn and CH₂Br-CO₂Et in PhMe yields (after hydrolysis) 1-keto-7-methoxy-2-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene-*b*, m.p. 119–120°, and a mixture of acids, which, heated with HI-P, then methylated (CH₂N₂), and finally heated with aq. NH₂Me yields a *substance*, C₂₀H₂₃O₃N, m.p. about 170° (softens 130–140°). 1-Keto-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene with HCO₂C₅H₁₁ and NaOEt in Et₂O yields 1-keto-7-methoxy-2-hydroxymethylene-1:2:3:4:9:10-hexahydrophenanthrene, m.p. 90–91°, whilst (I) and HCO₂Et similarly give 1-keto-7-methoxy-2-hydroxymethylene-1:2:3:4:9:10:11:12-octahydrophenanthrene, m.p. 140–141°. Me γ -(6-methoxy-3:4-dihydro-1-naphthyl)butyrate and β -carbomethoxypropionyl chloride with AlCl₃ in CS₂ yield an *acid*, C₁₉H₂₄O₆, m.p. 163–164°, probably γ -(6-methoxy-7- β -carboxypropionyl-1:2:3:4-tetrahydro-1-naphthyl)butyric acid, and an *acid*, C₁₉H₂₀O₆, m.p. 155–157°, probably γ -(6-methoxy-5- β -carboxypropionyl-1-naphthyl)butyric acid, which with HI yields 7-hydroxy-1-keto-1:2:3:4-tetrahydrophenanthrene.

J. D. R.

Synthesis of 10-hydroxy-4-keto-1:2:3:4-tetrahydrophenanthrene. G. HABERLAND and G. KLEINERT (Ber., 1938, 71, [B], 470–473).—3:2-OMe-C₁₀H₆-CO₂H is transformed by the successive actions of SOCl₂ in C₆H₆ and CH₂N₂ in Et₂O into 3-methoxy-2-diazoacetylnaphthalene, m.p. 98°, converted by halogen acid or AcOH into 5:6-benzocoumaranone, m.p. 146°. Condensation of 3:2-OMe-C₁₀H₆-COCl with CO₂Et-CH₂-CNAC-CO₂Et and treatment of the product with dil. NaOH and dil. H₂SO₄ gives β -3-methoxy-2-naphthylpropionic acid, m.p. 164° [*Me* ester, m.p. 87° (2:4-dinitrophenylhydrazon, m.p. 216°)]. This is reduced to γ -3-methoxy-2-naphthyl-*n*-butyric acid, m.p. 98°, cyclised by P₂O₅ in boiling C₆H₆ to 4-keto-10-methoxy-1:2:3:4-tetrahydrophenanthrene, b.p. 165°/1 mm., m.p. 87° (*semicarbazone*, m.p. 196°; 2:4-dinitrophenylhydrazon, m.p. 269°; *oxime*, m.p. 160°), which with boiling 48% HBr-AcOH gives 10-hydroxy-4-keto-1:2:3:4-tetrahydrophenanthrene, b.p. 155–165°/1 mm., m.p. 226° (*oxime*, m.p. 178°). H. W.

[**Benzanthrone.**] R. SCHOLL (Ber., 1938, 71, [B], 400–407).—Reply is made to Lauer (A., 1935, 1125). Repetition of previous work establishes the incorrectness of the statement of Clar *et al.* (A., 1932, 1134) that dihydrobenzanthrone (I), sensitive to air, is not formed by the reduction of benzanthrone (II) in alkaline medium (Na₂S₂O₄; Zn dust and NaOH), but that the first isolable product is a stable tetrahydrobenzanthrone (III). The ease of reduction of (II) depends greatly on its state of division but occurs readily with material pptd. from C₅H₅N by aq. NH₃ or NaOH. Too drastic treatment leads to (III). Disproportionation of (I) into (II) and (III) takes place only under energetic conditions. H. W.

Stearates of hydroxydibenzanthrones.—See B., 1938, 256.

Synthesis of substances related to sterols.
XVIII. D. A. PEAK and R. ROBINSON (J.C.S., 1937, 1581—1591; cf. A., 1936, 989).—2-Ketodecahydrochrysene-A (I) with H_2 -Pd-SrCO₃ in dry EtOAc gives 2-keto-1:2:3:4:5:6:7:8:13:14:15:16-dodecahydrochrysene-A (II), m.p. 147—148° [semicarbazone, m.p. 231—233° (cf. *loc. cit.*)], and when reduced (Pd-H₂-SrCO₃-MeOH) and the crude product oxidised with CrO₃ yields (II) and a new isomeride, 2-keto-1:2:3:4:5:6:7:8:13:14:15:16-dodecahydrochrysene-C, m.p. 87—88° (oxime, m.p. 186—187.5°). Reduction (H₂-Pd-SrCO₃-MeOH) of 2-ketodecahydrochrysene-B (III) gives 2-hydroxy-1:2:3:4:5:6:7:8:13:14:15:16-dodecahydrochrysene-γ, m.p. 155—156°, converted by NaOEt-EtOH (sealed tube; 6 hr.) into the isomeride-δ, m.p. 162—163°. Both isomeride-γ and -δ when oxidised with AcOH-CrO₃ give 2-keto-1:2:3:4:5:6:7:8:13:14:15:16-dodecahydrochrysene-B, m.p. 114—115° (oxime, m.p. 166—167°), converted into its isomeride (II), when heated with NaNH₂-C₆H₆. Similarly (III) is converted into (I). Reduction (Wolff-Kishner) of the semicarbazone of ketodecahydrochrysene-A gives the expected dodecahydrochrysene, m.p. 83—84°; the previously described specimen (*loc. cit.*) was probably not homogeneous. (II) with KOBu⁺-Bu⁺OH-Et₂O and MeI, gives 2-keto-16-methyl-1:2:3:4:5:6:7:8:13:14:15:16-dodecahydrochrysene, m.p. 122—122.5° [oxime, m.p. 222—224°; semicarbazone (IV), m.p. 245—247°]. NaOEt converts (IV) into 16-methyl-1:2:3:4:5:6:7:8:13:14:15:16-dodecahydrochrysene, m.p. 87—87.5°, dehydrogenated by Se (320—330°; 20 hr.) to chrysene, but not by Pt-black and only slowly by Pd-C. 6-Methoxy-α-tetralone (V) (improved prep.) with NaNH₂ in Et₂O and N₂ followed by acetylcyclopentene gives 3-keto-7-methoxy-3:4:9:10:11:12-tetrahydro-1:2-cyclopentanophenanthrene-B (VI), m.p. 123—124°, and -C, m.p. 167—169°; together with the compound, m.p. 194—195°, previously obtained (A., 1935, 1498) and now designated as isomeride-A (VII). The absorption spectra indicate that these three substances are stereoisomerides. Catalytic hydrogenation of (VII) gives 3-keto-7-methoxy-3:4:9:10:11:12-hexahydro-1:2-cyclopentanophenanthrene-α, m.p. 147—148°, which with KOBu⁺-Bu⁺OH-Et₂O and MeI gives 3-keto-7-methoxy-2-methyl-3:4:9:10:11:12-hexahydro-1:2-cyclopentanophenanthrene-α, m.p. 68—69°. Similarly (VI) gives 3-keto-7-methoxy-3:4:9:10:11:12-hexahydro-1:2-cyclopentanophenanthrene-β, m.p. 118—118.5° (dinitrophenylhydrazones, m.p. 193—194°), and 3-keto-7-methoxy-2-methyl-3:4:9:10:11:12-hexahydro-1:2-cyclopentanophenanthrene-β, m.p. 75—76° (dinitrophenylhydrazones, m.p. 171—172°), the semicarbazone, m.p. 226—227°, of which is readily formed and with NaOEt-EtOH (180°; 20 hr.) gives 7-methoxy-2-methyl-3:4:9:10:11:12-hexahydro-1:2-cyclopentanophenanthrene (VIII), m.p. 55—55.5°, b.p. 183°/2 mm., stereoisomeric with cestatriene Me ether

(Cook *et al.*, A., 1934, 404). Dehydrogenation of (VIII) with Se (300—320°; 5 days) gives 1:2-cyclopentanophenanthrene. The removal of the OMe group is considered to be due to the action of H₂Se. 7-Hydroxy-3-keto-3:4:9:10:11:12-tetrahydro-1:2-cyclopentanophenanthrene, m.p. 249°, obtained from the 7-OEt derivative (A., 1936, 989) and AlBr₃ in C₆H₆, is catalytically reduced to 7-hydroxy-3-keto-3:4:9:10:11:12-hexahydro-1:2-cyclopentanophenanthrene, m.p. 187—189° (decomp.). β-Furylisonopropenyl Me ketone (IX) and sodio-α-tetralone (X) in Et₂O afford 3-keto-1-furyl-2-methyl-1:2:3:9:10:11-hexahydrophenanthrene, m.p. 137.5—138° [also obtained from α-tetralone, KOBu⁺-Bu⁺OH, and (IX), but in inferior yield], which is hydrogenated (Pd-SrCO₃) to 3-hydroxy-1-furyl-2-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene, m.p. 140—140.5°. An attempt to open the furan ring by bromination and subsequent removal of Br was unsuccessful. Et ethylideneacetoacetate and (X) in Et₂O give 3-keto-1-methyl-1:2:3:9:10:11-hexahydrophenanthrene, m.p. 119—120°, b.p. 181—190°/1 mm., also obtained from the appropriate components and KOBu⁺-Bu⁺OH. Hydrolysis of Et γ-carbethoxypropylideneacetoacetate (XI) (A., 1936, 989) with 10% HCl gives γ-carboxypropylideneacetone, b.p. 160—166°/13 mm. (p-phenylphenacyl ester, m.p. 93—94°). Condensation of (XI) with (X) in Et₂O gave a fraction, b.p. 190—200°/0.8 mm., from which an acidic substance, C₁₄H₁₄O₇, m.p. 202.5—203.5° (sinters at 196°) (dinitrophenylhydrazones, m.p. 205—207°), was separated. The residue when treated with Brady's reagent gave an azo-derivative (?), C₂₅H₂₈O₇N₄, m.p. 183—184°. No cryst. derivatives could be obtained from the products obtained in the attempted condensation of (V) and (XI). CH₂Ph·CH₂·CHO, Ac₂O, and CH₂Ac·CO₂Et at 100° (24 hr.) afford Et γ-phenylpropylideneacetoacetate, b.p. 140—143°/0.1 mm., which with (X) yields a substance, m.p. 130.5—131°, and a liquid mixture, b.p. 205—245°/1 mm. (decomp.), from which no cryst. derivatives could be obtained. Attempted condensations of Et 2-methylcyclopentanone-3-carboxylate [modified prep. from Et α-cyano-α'-methylsuccinate, new b.p. 150—153°/17 mm.] with diethylaminobutanone methiodide failed. 2-Methylcyclopentanone-3-carboxyldiethylamide (dinitrophenylhydrazones, m.p. 199—199.5°) has b.p. 117—119°/0.1 mm. β-Chloro-ζ-methylheptane, b.p. 74—75°/35 mm., and β-iodo-ζ-methylheptane, b.p. 83°/14 mm., gave Grignard reagents which gave no lactonic products with Et β-formylpropionate. Attempts to introduce the residues of CHMeBr·CO₂Et and CH₂Cl·CH₂CO₂Et into CH₂Ac·CO₂Et failed in whichever order the condensations were carried out. Et Δ¹-dihydrocitronellylideneacetate, b.p. 128—131°/10 mm., obtained from the acid, with Et₂C₂O₄ and K in C₆H₆ gives a product which decomposes on distillation; catalytic reduction and distillation (with decomp.) gives a substance, C₁₇H₃₂O₄, b.p. 131—136°/0.4 mm. Et dihydrocitronellate [prepared from the acid (XII)] with MgPhBr-Et₂O gives 60-diphenyl-β-ζ-dimethyl-Δ⁷-octene, which with AcOH-CrO₃ gives nordihydrocitronellal acid (XIII), b.p. 127—129°/10 mm. The acid chloride, b.p. 71—71.5°/8 mm., of this reacts with

Et sodioacetylsuccinate, but on hydrolysis of the resulting ester (XIII) was recovered, no β -nordihydrocitronelloylpropionic acid being obtained. The *semicarbazone* of a keto-acid, b.p. 175—188°/5 mm., derived by the same method from (XII) [in the (XIII) used], has m.p. 156—157°.

H. G. M.

Ketone from the urine of pregnant mares. R. D. H. HEARD (J. Amer. Chem. Soc., 1938, 60, 493—494).—The non-phenolic extract of this urine yields pregnanetriol, a H_2O -sol. *semicarbazone*, m.p. 253—254° (decomp.), and a saturated ketone, $C_{18-20}H_{24-28}O_3$, m.p. 252° (sinters at 249°) [insol. *monosemicarbazone*, m.p. variable, 300—315° (decomp.); no acetate].

R. S. C.

Derivatives of the ovarian hormone active by mouth. 17-Ethinyl-œstradiol and pregnenin-17-ol-3-one. H. H. INHOFFEN and W. HOHLWEG (Naturwiss., 1938, 26, 96).—17-Ethinylœstradiol, m.p. 145—146°, $[\alpha]_D +1^\circ$ in dioxan, when administered orally acts on castrated rats in doses of 3×10^{-6} g. *Pregnenin-17-ol-3-one*, m.p. 264—266°, $[\alpha]_D +21.5^\circ$ in dioxan, administered to immature rabbits previously treated with follicular hormone, is active in doses of 2 mg. (subcutaneously) and 4 mg. (orally).

W. O. K.

Enol esters of 3-carbonyl derivatives of sterols.—See B., 1938, 320.

Michael reaction. III. General considerations: addition of alkylmalonic esters to unsaturated diketones. J. A. GARDNER and H. N. RYDON (J.C.S., 1938, 45—48).—The normal reaction of $CR_2 \cdot CR'X$ ($X = CO_2Et$, COR, CN) with $CHR''(CO_2Et)_2$ gives $CHR'X \cdot CR_2 \cdot CR''(CO_2Et)_2$ (I), and the abnormal reaction, with migration of alkyl, either $CO_2Et \cdot CR'X \cdot CR_2 \cdot CHR'' \cdot CO_2Et$ (II) (cf. Holden and Lapworth, A., 1931, 1271) or $CR'R''X \cdot CR_2 \cdot CH(CO_2Et)_2$ (III) (cf. Thorpe, J.C.S., 1900, 77, 923). Acid hydrolysis of (I) and (II) gives $CHR'X \cdot CR_2 \cdot CHR'' \cdot CO_2H$ ($X' = CO_2H$, COR) and of (III), $CR'R''X \cdot CR_2 \cdot CH_2 \cdot CO_2H$. *trans*-($CH \cdot CPh$)₂ (IV) with $EtOH \cdot NaOEt$ gives (probably) 1:4:5-*tribenzoyl-2-phenylcyclopentadiene* (V), m.p. 161°, since *cis*-($CPh \cdot CPh$)₂ (VI) does not react with $NaOEt$. (VI) does not react with $CH_2Ph \cdot CH(CO_2Et)_2$ (VII), but (IV) gives *Et*₂ $\gamma\delta$ -*dibenzoyl- α -phenyl-n-butane- $\beta\beta$ -dicarboxylate*, m.p. 92° [synthesised from $COPh \cdot CH_2 \cdot CHCl \cdot CPh$ and (VII)], the addition being normal. ($CH \cdot COMe$)₂ [from ($CHAc \cdot CO_2Et$)₂ (improved prep.) by conversion into ($CH_2 \cdot COMe$)₂ and dehydrogenation] with $NaOEt$ gives tarry products and with $CHNa(CO_2Et)_2$, a ketonic oil (*semicarbazone*, m.p. 186—187°) probably analogous to (V).

E. G. B.

Reductions of $\alpha\beta$ -bistrimethylbenzoyl ethylene oxide. R. E. LUTZ and J. L. WOOD (J. Amer. Chem. Soc., 1938, 60, 229—235).—The action of reducing agents on $\alpha\delta$ -diketo- $\alpha\delta$ -dimesitylbutylene $\beta\gamma$ -oxide (I), m.p. 73.5—74.5°, differs in some respects from that of the Ph_2 analogue. *trans*- $\alpha\delta$ -Diketo- $\alpha\delta$ -dimesityl- Δ^8 -butene (II), prepared from $s\text{-}C_6H_5Me_3$, fumaryl chloride, and $AlCl_3$, with hot $HCl \cdot AcOH$ gives erratically β -chloro- $\alpha\delta$ -diketo- $\alpha\delta$ -dimesitylbutane, m.p. 74°, re-solidifying with m.p. 130°, reconverted at 100° or

in hot $EtOH$ into (II); with $H_2O_2 \cdot NaOH \cdot EtOH$ at 65° it affords (I), stable to $AcCl \cdot H_2SO_4$, resinified by PCl_5 , and converted by $NaOMe$ or, better, HCl in various solvents into β -chloro- $\alpha\delta$ -diketo- $\alpha\delta$ -dimesityl- Δ^8 -butene (III), m.p. 113—113.5°, and the β -enol (IV) of $\alpha\beta\delta$ -triketo- $\alpha\delta$ -dimesitylbutane [also obtained from (III) by $NaOH \cdot aq. MeOH$]. $CrCl_2$ and $Na_2S_2O_4$ have no effect on (I). $KI \cdot AcOH$ reduces (I) to (II). I and red P in hot $AcOH$ give $(C_6H_5Me_3 \cdot CO \cdot CH_2)_2$ (V), obtained also from (III) by $H_2 \cdot Pt$ in $EtOH$. $Zn \cdot NH_4Cl \cdot EtOH$ affords β -hydroxy- $\alpha\delta$ -diketo- $\alpha\delta$ -dimesitylbutane (VI), m.p. 91—92°, and a little (?) α -hydroxy- δ -keto- $\alpha\delta$ -dimesitylbutylene $\beta\gamma$ -oxide (VII), m.p. 119.5—120°. The structure of (VI), which is best obtained by Raney Ni with some (V), is proved by conversion by $HCl \cdot EtOH$ into (II), by $AcCl$ into its acetate, m.p. 85.5—87.5°, by $Ac_2O \cdot H_2SO_4$ into 3-acetoxy-2:5-dimesitylfuran, m.p. 100—101° [obtained from (II) by $AcCl \cdot H_2SO_4$], by $NaOH \cdot MeOH$ into (II) or (IV) and (V), by reduction (I-red P- $AcOH$) to (V), and by dehydration by $HCl \cdot Et_2O$ and subsequent fusion to (II). HI converts (VII) into $C_6H_5Me_3 \cdot CH_2 \cdot CO \cdot [CH_2]_2 \cdot C_6H_5Me_3$ (VIII) and H_2 -Raney Ni gives a substance, $C_{22}H_{30}O_3$, m.p. 160°, but other reagents are without effect or give resins. Pyrolysis of $C_6H_5Me_3 \cdot CH(OH) \cdot CO \cdot CH_2 \cdot C(OH) \cdot C_6H_5Me_3$ gives the same products, viz., (IV) and, in absence of air, (V), as does that of (VI), showing existence of a complex keto-enol tautomeric system. H_2 -Raney Ni has no effect on (V) or (VII), which are thus produced by independent reactions. PtO_2 in large excess in $EtOH$ brings about addition of only 2 H to (I) (must be pure), reducing a CO and giving α -hydroxy- δ -keto- $\alpha\delta$ -dimesitylbutylene $\beta\gamma$ -oxide, m.p. 129.5° (*phenylurethane*, m.p. 155—156°), which is reconverted into (I) by CrO_3 , with $KI \cdot AcOH$ in N_2 gives 2:5-dimesitylfuran, with I-red P- $AcOH$ affords (VIII) and a small amount of an enolic substance, and with H_2 -Raney Ni gives 75% of δ -hydroxy- α -keto- $\alpha\delta$ -dimesitylbutane, m.p. 132—133° [oxidised by CrO_3 to (V)], and 11—20% of $\gamma\delta$ -dihydroxy- α -keto- $\alpha\delta$ -dimesitylbutane, m.p. 162—163° (converted into dimesitylfuran by I-red P- $AcOH$ or $HCl \cdot Et_2O$). $Zn \cdot AcOH$ at 50° reduces (I) in poor yield to (VI). $Na \cdot EtOH$ reduces (I) to $[C_6H_5Me_3 \cdot CH(OH) \cdot CH_2]_2$. M.p. are corr.

R. S. C.

Cyclic acetals of mono- and di-carbonyl compounds. J. BÖESEKEN and F. TELLEGEN [with J. F. GREUP, F. A. IN 'T VELD, P. WIJGA, M. STAP, H. KELDER, J. P. EHRENBURG, F. WIJBRANS, L. TEEPE, F. TOLLENAAR, G. D. DEKKER, and C. VAN DER MEULEN] (Rec. trav. chim., 1938, 57, 133—143).—Cyclic acetals are prepared, generally by the action of conc. H_2SO_4 (occasionally P_2O_5) on a mixture of a diol and a mono- or di-ketone. It is noteworthy that while cyclohexanone (*Et*₂ acetal, b.p. 78—85°/18 mm.) with $(CH_2 \cdot OH)_2$ and $CH_2(CH_2 \cdot OH)_2$ gives the acetals, $C_6H_{10} \begin{smallmatrix} <O \cdot CH_2 \\ <O \cdot CH_2 \end{smallmatrix}$, b.p. 67—74°/20 mm., and $C_6H_{10} \begin{smallmatrix} <O \cdot CH_2 \\ <O \cdot CH_2 \end{smallmatrix} CH_2$, b.p. 95—102°, m.p. 34°, respectively, cyclopentanone (*Et*₂ acetal, b.p. 63—65°/20 mm.) does not react with either glycol. Ac_2 (modified prep.), $(CH_2 \cdot OH)_2$, and conc. H_2SO_4 (varying

amounts) give the *monoacetal* (I), $\text{COMe} \cdot \text{CMe} \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \text{O} \cdot \text{CH}_2 \end{smallmatrix}$, b.p. 75–77°/17 mm., and two *diacetals*, (II), b.p. 103–105°/17 mm., m.p. 90–92°, and (III), $(\text{CMe} \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \text{O} \cdot \text{CH}_2 \end{smallmatrix})_2$, b.p. 90–92°/13 mm., m.p. 30–31°; (II) and (III) are similarly obtained from (I) but with P_2O_5 , (I) and $(\text{CH}_2\text{OH})_2$ yield (III). (II) is a *trans*-naphthodioxan since it has no dipole moment. Ac_2 and $\text{CH}_2(\text{CH}_2\text{OH})_2$ yield the *acetal*, $\text{COMe} \cdot \text{CMe} \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \text{O} \cdot \text{CH}_2 \end{smallmatrix} \text{CH}_2$, b.p. 82°/16 mm., whilst Ac_2 and $(\text{CHMeOH})_2$ give a *diacetal*, m.p. 87–88.5°. The *diacetals* from $(\text{CH}_2\text{OH})_2$ and benzil, $\text{COPh} \cdot \text{COMe}$, and BzCHO have m.p. 183–185°, 162–164°, and 78°, respectively; the *diacetal* from AcCHO has b.p. 95–110°.

Δ^4 -Pregnene-3 : 20-dione.—See B., 1938, 320.

Structure of corticosterone. M. STEIGER and T. REICHSTEIN (Nature, 1938, 141, 202).—Corticosterone (I) can be transformed into *allopregnane*, m.p. 84°, $[\alpha]_D^{25} +12.7^\circ$ in CHCl_3 , also obtained by Clemmensen reduction of *allopregnane*-3 : 20-dione. This appears to prove the presence of a steroid structure in (I).

Testosterone, the crystalline male hormone from ox testes. II. K. DAVID (Acta brev. neerl. Physiol., 1935, 5, 108–109; Chem. Zentr., 1936, ii, 322; cf. A., 1936, 1156).—Oxidation of testosterone with CrO_3 yields androstenedione (I). A second form of (I), m.p. 142–144°, is isolated by crystallisation from COMe_2 . Recrystallisation from hexane causes transition to the form of m.p. 172–173°.

Sex hormones and related substances. X. Production of progesterone and androstenedione by oxidation of cholestenone. W. DIRSCHERL and F. HANUSCH (Z. physiol. Chem., 1938, 252, 49–52; cf. A., 1936, 1157).—Cholestenone with CrO_3 in AcOH at 45–50° gives progesterone and androstenedione. Oxidation of cholestanone gives androstenedione.

Electrometry and ultra-violet spectrography of rhodizonic acid; its iodine titre. G. CARPÉNI (Compt. rend., 1938, 206, 432–435).—Electrometric titration shows the presence of two groups with acidic function; $p_{K_1} = 3.15$ and $p_{K_2} = 4.9$. The absorption spectrum contains five bands, varying in intensity with the p_H ; the origins are indicated. Titration with I shows that the α -enediol form (I) is stable in acid solution, but disappears in alkaline solution. The I oxidation product (tri-quinoyl) is unstable, re-forming rhodizonic acid on keeping in solution.

Influence of pyrocatechol on the stability of o-benzoquinone in aqueous solution. C. R. DAWSON and J. M. NELSON (J. Amer. Chem. Soc., 1938, 60, 245–249).—The rate of disappearance of $\text{o-C}_6\text{H}_4\text{O}$ from mixtures of $\text{o-C}_6\text{H}_4(\text{OH})_2$ and quinone

at p_H 4–5.5 is measured by titration with I. The concns. and initial ratio of quinone to $\text{o-C}_6\text{H}_4(\text{OH})_2$ are varied at will by starting from a known wt. of the latter and adding an amount of $\text{Ce}(\text{SO}_4)_2$ sufficient to give the required amount of quinone. The rate of disappearance of quinone is $\propto [\text{OH}]^2$, is accelerated by increasing amounts of $\text{o-C}_6\text{H}_4(\text{OH})_2$, and is of the first order only in very dil. solution.

[Preparation of] p-benzoquinone. H. N. MCCOY (J. Chem. Educ., 1937, 14, 494).—Quinol (10 g.), KBrO_3 (5.5 g.), H_2O (100 ml.), and $\text{N-H}_2\text{SO}_4$ (5 ml.) are warmed to 60°; after 10–15 min. the mixture is heated to 80° to dissolve the quinone, cooled to 0°, filtered, washed free from KBr with H_2O , and dried. No by-products are formed, and the quinone is exceptionally pure. The amount of H_2SO_4 appears to be crit.

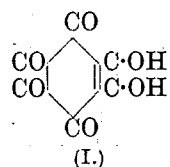
Action of magnesium phenyl bromide on anthraquinones. C. F. H. ALLEN and R. W. MCGIBBON (Canad. J. Res., 1938, 16, B, 35–36).—In agreement with Kovache (cf. A., 1918, i, 539) it is suggested that low yields of diol from anthraquinones are due to the slight solubility of the latter in Et_2O together with pptn. of the Mg complex on the larger particles. By using Bu_2O , in which anthraquinone (I) is much more sol., the yield of diol is raised to 80%; with 2-methylanthraquinone (II), which is even more sol., no (II) was recovered and the yield of diol was 86% (66% in Et_2O). The procedure is: Et_2O -MgPhBr is treated with (I) followed by Bu_2O ; the mixture is heated at 100–105° (Et_2O allowed to distil off) in an inert atm. Bu_2O is more suitable than PhMe for forced Grignard reactions. No evidence was obtained of 1 : 4 addition of MgPhBr.

4 - C - Alkylanilino - 1 - alkylaminoanthraquinones.—See B., 1938, 258.

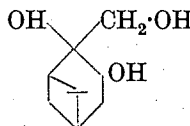
New product with odour of amber. V. ISAEV (Maslob. Shir. Delo, 1937, No. 6, 22).—*Dihydrocarveyl benzoate*, b.p. 191–195°/15 mm., $d_{25}^{25} 1.029$, $n_D^{25} 1.5237$, has an odour of amber, and may replace sandal oil in perfumes.

Action of selenium dioxide on nopinene. W. ZACHAREWICZ (Rocz. Chem., 1937, 17, 630–641).—*l*-Nopinene (I), heated at the b.p. with SeO_2 , yields *d*-pinocarveol, pinocarvone, *d*-pinocarvyl selenide, and *l*-myrtenyl selenide, $[\alpha]_D -18.26^\circ$ in COMe_2 , identical with that obtained from *l*-pinene, into which (I) largely isomerises under the conditions of the experiment. Oxidation of *l*-myrtenol or α -pinocarveol with KMnO_4 in COMe_2 gives the substituted *d*-glycerol (II), m.p. 67–68°, $[\alpha]_D -10.55^\circ$ in COMe_2 (*xy*-diacetate, m.p. 114–115°, $[\alpha]_D -11.27^\circ$ in COMe_2). Similarly *d*-myrtenol gives the *d*-glycerol, which with (II) affords the *racemate*, m.p. 71–71.5° (*xy*-diacetate, m.p. 91.5–92.5°).

Oxidation in the terpene series. I. Action of lead tetra-acetate and of red lead and acetic acid on pinene, dipentene, α -terpinene, and terpinolene. K. WARD, jun. (J. Amer. Chem. Soc., 1938,



(I.)



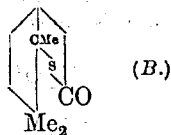
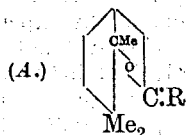
(II.)

60, 325—327).— $\text{Pb}(\text{OAc})_4$ or $\text{Pb}_3\text{O}_4\text{--AcOH}$ converts the terpenes named into mixtures of (a) hydrocarbons, (b) acetates of monohydric alcohols, (c) monoacetates of dihydric alcohols, and (d) products of higher b.p. (? polymerisation products and higher acetates). $\text{Pb}(\text{OAc})_4$ gives a higher ratio, (a) : (b), and (b) has a higher ester val. With Pb_3O_4 pinene gives mainly sobrerol, which is obtained by $\text{Pb}(\text{OAc})_4$ only in AcOH and then in poor yield. R. S. C.

New series of camphene derivatives. S. S. NAMETKIN and A. S. ZABRODINA (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 1015—1033).—The work of the authors (A., 1925, i, 416; 1926, 521; 1927, 249; 1928, 1018; 1937, II, 108) is reviewed. R. T.

Optical rotation and racemisation in the camphene rearrangement. II. Change in optical activity in dehydration of substituted *tert*-bornyl alcohols. A. I. SCHAVRIGIN (J. Gen. Chem. Russ., 1937, 7, 2668—2677).—*tert*-Methylbornyl alcohol, $[\alpha]_D +12.66^\circ$, when dehydrated by heating with KHSO_4 yields α -methylcamphene, $[\alpha]_D +15.8^\circ$, which, prepared analogously from *tert*-methylfenchyl alcohol, has $[\alpha]_D +14.7^\circ$ (A., 1937, II, 67). It is concluded that inversion of optical rotation is associated only with structural rearrangements, not with dehydration alone. This view is confirmed by the known results of dehydrating *tert*-phenyl-, -benzyl-, -propyl-, and -allyl-bornyl alcohol (I). When heated with KHSO_4 (3 hr. at $160\text{--}165^\circ$), (I) affords α -allylidene camphor, b.p. $95\text{--}97^\circ/13\text{ mm.}$, $[\alpha]_D -95.47^\circ$. $[\alpha]_D$ are for EtOH solution. R. T.

isoAminocamphor. Y. ASAHINA and T. TUKAMOTO (Ber., 1938, 71, [B], 305—311).—*iso*Aminocamphor (I), m.p. 39° , obtained by the action of HI on camphoroxime, gives an *oxalate*, m.p. 148° , a *hydrochloride* (II), m.p. 89° , which in H_2O slowly passes into dihydrocamphenolactone (III), b.p. $116^\circ/10\text{ mm.}$, m.p. 30° , and an α -semicarbazone, m.p. 170° . $\text{NH}_2\text{OH.HCl}$ and (II) in dil. KOAc-EtOH give the oxime, two forms, m.p. 171° (IV) and 111° (V), respectively. Dry distillation of (II) leads to β -camphenolamide, m.p. 86° . The β -hydroxycamphor obtained by Forster and Howard (J.C.S., 1913, 103, 63) by the action of $\text{H}_2\text{C}_2\text{O}_4$ on dihydrocamphenolactonesemicarbazone still contains semicarbazide since with 30% NaOH it gives a *ppt.* of $\text{C}_{11}\text{H}_{20}\text{O}_3\text{N}_3\text{Na}$, m.p. 185° or $(+1\text{H}_2\text{O})$ m.p. 160° . (I) gives a PhSO_2 derivative, m.p. 108° , converted by 5% KOH at 100°

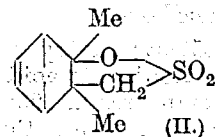
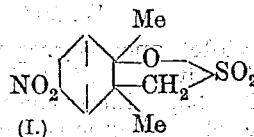


into (III) and PhSO_2NH_2 thus suggesting that (I) is A (R = NH). This possibility is strengthened by its conversion by H_2S in Et_2O into dihydro- β -camphenolthionlactone (VI) (A; R = S), m.p. 60° , hydrolysed by 10% HCl mainly to H_2S and (III) and transformed by NH_2OH into (IV) and (V). α -Camphenol-enitrile is converted by EtOH and HCl in Et_2O into α -camphenol-imino ether, b.p. $123^\circ/42\text{ mm.}$ (*semicarbazone*, m.p. 165°), transformed by H_2S into *Et*

camphenolthionate, b.p. $106\text{--}107^\circ/5\text{ mm.}$ Similarly β -camphenolnitrile gives successively β -camphenol-imino ether, b.p. $109\text{--}111^\circ/14\text{ mm.}$ (*semicarbazone*, m.p. 180°), and *Et* β -camphenolthionate, b.p. $127^\circ/20\text{ mm.}$ Either ester is rapidly converted by HI (*d* 2.00) at 100° into dihydrocamphenolthiol-lactone (B), m.p. 58° , which does not evolve H_2S when heated with 10% HCl and is not identical with (VI). H. W.

Action of sulphuric acid on camphene. Y. ASAHINA, T. SANO, and T. MAYEKAWA [in part with H. KAWAHATA] (Ber., 1938, 71, [B], 312—317).—2-Hydroxycamphane- ω -sulpholactone (I), m.p. 133° , is obtained by the action of $\text{Ac}_2\text{O--H}_2\text{SO}_4$ on optically inactive camphene, by the method of Lipp and Holl (A., 1929, 570) from 2-hydroxycamphane- ω -sulphonic acid (II), and from 2-hydroxycamphane- π -sulphonic acid (III) so that (I) does not result from (II) by simple loss of H_2O but by a complex isomerisation. (II) is a saturated compound which gives a salt, $\text{C}_{10}\text{H}_{17}\text{O}_4\text{SK}$, which affords only a trace of (I) when boiled with HCl whereas the product of the hydrolysis of (I) is an unsaturated substance which gives a *K* salt, $\text{C}_{10}\text{H}_{15}\text{O}_3\text{SK}$, yielding much (I) when boiled with HCl. It is therefore probable that OH of the sulphonic acid corresponding with (I) is *tert*. and is lost as H_2O during hydrolysis. The formation of optically inactive (I) from optically active (II) can be explained only by assumption of the intermediate formation of tricyclic- ω -sulphonic acid. The production of (I) from (III) is probably due to a Wagner-Nametkin isomerisation to (II) or to direct conversion into camphene- π -sulphonic acid through a tricyclic- π -sulphonic acid. The fresh mother-liquors from the prep. of Reychler's sulphonic acid contain the *acetoxysulpholactone*, $\text{C}_{12}\text{H}_{18}\text{O}_8\text{S}$, m.p. 178° , $[\alpha]_D \pm 0^\circ$, whilst from older mother-liquors a substance, m.p. $156\text{--}158^\circ$, $[\alpha]_D -25.0^\circ$ in EtOH, is also isolated. H. W.

Action of sulphuric acid on nitrocamphenes. Y. ASAHINA and K. YAMAGUTI (Ber., 1938, 71, [B], 318—324).—Optically inactive 6-nitrocamphene is transformed by conc. $\text{H}_2\text{SO}_4\text{--Ac}_2\text{O}$ at $>20^\circ$ into 5-nitrocamphenehydrato- π -sulpholactone (I), m.p. $133\text{--}134^\circ$. This is reduced (Pd-C in AcOH) to 5-amino-



camphenehydrato- π -sulpholactone, a liquid not volatile without decomp. (*Bz* derivative, m.p. 190°), converted by diazotisation into the *dehydroisomulpholactone*, m.p. 197° , reduced (Pd-C in EtOH) to the saturated *isomulpholactone*, m.p. 168° . 1-Nitrocamphene similarly gives 4-nitrocamphenehydrato- π -sulpholactone, m.p. 258° , $[\alpha]_D^{25} -5.15^\circ$ in CHCl_3 , reduced to 4-aminocamphenehydrato- π -sulpholactone (III), m.p. $75\text{--}76^\circ$ [*hydrochloride*, m.p. 255° (decomp.)]; *Bz* derivative, m.p. 208.5° , $[\alpha]_D^{25} +16.34^\circ$ in EtOH; this when diazotised gives the partly cryst. 4-hydroxycamphenehydrato- π -sulpholactone [*acetate*, m.p. 186° (decomp.)], $[\alpha]_D^{25} +28.30^\circ$ in CHCl_3 . When boiled with 10% HCl (III) passes into 4-aminocamphene- π -sulphonic acid [*Na* ($+2\text{H}_2\text{O}$) salt]. This

salt when diazotised yields 4-hydroxycamphene- π -sulpholactone, m.p. 115—116°, $[\alpha]_D^{25}$ -12.86° in EtOH [hydrochloride, m.p. 175—176° (decomp.), $[\alpha]_D^{25}$ -1.92° in EtOH], reduced (Pd-C in AcOH) to 4-hydroxydihydrocamphene- π -sulpholactone, m.p. 143°, $[\alpha]_D^{25}$ +4.93° in EtOH, or m.p. 147°. This is oxidised by BzO_2H in Et_2O to the corresponding oxide (IV) $\text{C}_{10}\text{H}_{14}\text{O}_4\text{S}$, two forms, m.p. 172°, $[\alpha]_D^{25}$ -14.79° in CHCl_3 , and m.p. 153°, $[\alpha]_D^{25}$ -8.47° in CHCl_3 , respectively. Ozonolysis of (IV) yields the ketosulpholactone (V), m.p. 171—172°, $[\alpha]_D^{25}$ +47.25° in CHCl_3 (p-nitrophenylhydrazones, m.p. 230°).

H. W.

Catalytic oxidation of bornylamine. N. J. DEMJANOV and I. I. LENARSKI (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 1001—1013).—Bornylamine (I) in $\text{Pr}^{\text{iso}}\text{OH}$, oxidised by O_2 in presence of Cu, at 50—55°, gives chiefly camphor, with small amounts of bornylene, and traces of camphorazine (II). Camphoroxime (III) is not an intermediate product, as it is not oxidised under these conditions. Camphor is formed when (II), (III), or camphorimine (IV) is steam-distilled. The reaction of oxidation is represented: (I) \rightarrow (IV) \rightarrow (II) \rightarrow camphor.

R. T.

Dependence of optical rotatory power on chemical constitution. XV. Chloroaryl derivatives of stereoisomeric methylenecamphors. B. K. SINGH and B. BHADURI (Proc. Indian Acad. Sci., 1937, 6, A, 340—358).—The decrease in $[\alpha]$ which might be expected in view of the replacement of H by a negative group such as Cl in the C_6H_5 nucleus (Thomson, A., 1923, ii, 682) is realised by results which show that $[\alpha]$ for the monochloro-anilinomethylenecamphors is < for the parent compound in MeOH, EtOH, COMe_2 , CHCl_3 , C_6H_6 , and $\text{C}_5\text{H}_5\text{N}$ for 9 lines from Cd_{4800} to Li_{6708} . A progressive diminution in $[\alpha]$ is observed for 2:4-dichloro- (I) and 2:4:6-trichloro-anilinomethylenecamphor (II). The sequence of different substituent groups is $\text{H} > \text{Me} > \text{Cl}$ (cf. A., 1931, 1160) in agreement with the polar series deduced from electronic theory. The sequence of $[\alpha]$ of the position isomerides is $\text{H} > p > o > m$ in MeOH, EtOH, and $\text{C}_5\text{H}_5\text{N}$, $\text{H} > o > m > p$ in CHCl_3 and C_6H_6 , and $\text{H} > p > m > o$ in COMe_2 , the val. being always highest for the unsubstituted compound (cf. A., 1931, 848, 1160). $M[\alpha]_{D_{4800}}^{25}$ for o-chloroanilinomethylenecamphor (d- and l-, m.p. 103—104°; dl, m.p. 92—93°) is 400.2° in MeOH, 405.8° in EtOH, and 364.7° in $\text{C}_5\text{H}_5\text{N}$; for m-chloroanilinomethylenecamphor (d- and l-, m.p. 118—119°; dl, m.p. 114—115°) 388.5° in MeOH, 384.7° in EtOH, 363.6° in C_6H_6 , and 381.4° in CHCl_3 (the solution turning light pink on keeping but showing no mutarotation); for p-chloroanilinomethylenecamphor (d- and l-, m.p. 186—187°; dl, m.p. 185—187°) 417.7° in MeOH, 406.3° in EtOH, 359.4 \rightarrow 349.4° in 24 hr. in C_6H_6 , 374.6° \rightarrow 363.4° in 18 hr. in CHCl_3 ; for (I) (d- and l-, m.p. 122—123°; dl, m.p. 126—127°, true dl-form at least in solid state) 362.5° in MeOH, 369.3° in EtOH, and 337.9° in C_6H_6 ; for (II) (d- and l-, m.p. 108—109°; dl, m.p. 107—108°) 259.8° in MeOH, 265.2° in

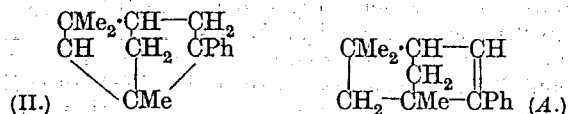
EtOH, and 219.1° in C_6H_6 . The numerical identity of $[\alpha]$ for optical isomerides is further confirmed.

R. G.

New salts of camphor-10-sulphonic acid. R. LENOCI (Boll. Chim. farm., 1938, 77, 41—45).—The following salts are described: p-phenetidine, m.p. 158—159°, $[\alpha]_D^{25}$ +15.33° (all rotations in H_2O), anaesthesia, (+ H_2O), m.p. 150—152°, $[\alpha]_D^{25}$ +14.43°, tutocaine [dimethyl-(γ -p-aminobenzoyloxy- β -methylbutyl)amine], m.p. about 100°, $[\alpha]_D^{25}$ +14.19°, and percaïne [α -butyloxycinchonin- β' -(diethylamino)-ethylamide] d-camphor-10-sulphonate, $[\alpha]_D^{25}$ +11.95°.

E. W. W.

Fenchene series. VII. 2-Phenylisofenchol and the phenylfenchenes derived therefrom. G. KOMPPA and G. A. NYMAN (Annalen, 1938, 533, 290—295).—isoFenchone reacts unsatisfactorily with MgPhBr , giving dl-2-phenylisofenchol (I), b.p. 163—165°/12 mm., m.p. 71—72°, which is quantitatively dehydrated by KHSO_4 at 160—170° to a mixture of hydrocarbons. Treatment of this with O_3 leaves (?)



2-phenylcyclofenchene (II), b.p. 127—128°/11 mm., unattacked. The portion attacked by O_3 does not react with $\text{NH}_2\text{CO}\cdot\text{NH}\cdot\text{NH}_2$. It is oxidised by alkaline KMnO_4 to 1-benzoyl-1:4:4-trimethylcyclopentane-3-carboxylic acid, m.p. 106—107° (oxime, m.p. 100—101.5°). Loss of H_2O from (I) occurs therefore with formation of (II) and 2-phenyl-8-fenchene (A) and without isomerisation. The partial incidence of a Wagner transformation during the dehydration of tert.-2-methylisofenchol must be regarded as a special case.

H. W.

Polyterpenes and polyterpenoids. CXXIII. Degradation of allobetulin and hydroxymethyleneallobetulin with chromium trioxide. L. RŮŽICKA, F. GOYAERT, M. W. GOLDBERG, and A. H. LAMBERTON (Helv. Chem. Acta, 1938, 21, 73—83).—Explanation is given of the production of two different Me esters from the acid (I) $\text{C}_{30}\text{H}_{46}\text{O}_5$ obtained by the oxidation of allobetulin (A., 1932, 749) and hydroxymethyleneallobetulin (II) (A., 1934, 529). Esterification of (I) by CH_2N_2 is greatly facilitated if the acid is dissolved in alkali and re-pptd. by acid; this is due only in part to the finer state of division. (I) is now shown to neutralise 2 mols. of alkali when boiled with $\text{NaOH}\cdot\text{EtOH}$, one being required by CO_2H and the other for the opening of the lactone ring. Protracted treatment of (I) in Et_2O , particularly in presence of MeOH, gives a product (III), $\text{C}_{32}\text{H}_{52}\text{O}_6$, m.p. 195—200° (decomp.) and, after re-solidification, m.p. about 230°, probably derived from the keto-hydroxydicarboxylic acid $\text{C}_{30}\text{H}_{48}\text{O}_6$, obtained by rupture of the lactone ring. It is possible, however, that it is the Me ester which retains 1 MeOH at 120°. Heating at 130—140° or crystallisation from dioxan causes loss of 1 MeOH, leaving a product, $\text{C}_{31}\text{H}_{48}\text{O}_5$ (IV), m.p. 230°. Neutralisation of (I) with 1 mol. of NaOMe and treatment of the product with MeI leads to (IV) in which the first m.p. 195° is not ob-

served if the substance has been heated at 130–140°. The second Me ester (V), $C_{31}H_{48}O_5$, obtained previously only from the acid derived from (II), is invariably obtained when the acid is first boiled with alkali for some time and then suitably esterified. In both series the acid $C_{30}H_{46}O_5$ is converted by boiling alkali followed by acidification, desiccation at 120°/high vac., and treatment with CH_2N_2 in Et_2O into the product, m.p. 260°, which contains 1 OMe (Zeisel). The re-pptd. acid is $C_{30}H_{48}O_6$ (VI); it is dibasic and hence is a ketohydroxydicarboxylic acid. It has m.p. >200° and, after re-solidification, m.p. 292–295° (corr.). During the initial melting the lactone ring is closed, possibly with re-formation of the initial acid. The Na_2 salt of (VI) when heated with MeI in MeOH passes into (V) so that closure of the lactone ring takes place during esterification. The differences in structure between (IV) and (V) are not completely elucidated. NH_2OH and (IV) give a product containing 2N in the mol. whereas under similar conditions (V) is unchanged. Similarly (I) and NH_2OH give a non-cryst. product from which a cryst. portion, (?) $C_{30}H_{48}O_3N_2$, m.p. 210°, is separated by solvents. $NH_2 \cdot CO \cdot NH \cdot NH_2$ and (I) from either source yield a substance, m.p. about 235°, which appears to contain 1 $N \cdot NH \cdot CO \cdot NH_2$ in the mol. The two carboxyls in $C_{30}H_{46}O_5$ must arise through ring fission at the position of OH in ring A of betulin (VI) since this is the only possibility by which the $CH \cdot OH$ of (II) can disappear. The possible intermediate production of a 1:2-(CO)₂ compound is not shown by the behaviour towards $o\text{-}C_6H_4(NH_2)_2$. Further the production of (I) involves the fission of the oxide ring of allobetulin, in the formation of which the original double linking and the primary OH of (VI) are involved. In the lactone ring of (I) a linking exists between one of the CO_2H and a C either involved in the original double linking or by the primary OH. It follows that the primary OH and the double linking in (VI) are present either in ring B or C.

H. W.

Polyterpenes and polyterpenoids. CXXIV.

Gypsogenic acid. L. RUZICKA, G. GIACOMELLO, and A. GROB (Helv. Chim. Acta, 1938, 21, 83–87).—Gypsogenin, after dissolution in aq. Na_2CO_3 and reprecipitation by acid followed by sublimation at 265°/high vac., has m.p. 272–275° without previous softening. The product, $C_{32}H_{47}O_6Br$, of the oxidation of acetyl-gypsogenin bromolactone with CrO_3 in H_2SO_4 (A., 1936, 1514; 1937, II, 201) is converted by debromination by Zn dust and AcOH followed by hydrolysis into gypsogenic acid (I), m.p. >380° (decomp.) [Ac derivative, m.p. 325° (decomp.); Me₂ ester (II), m.p. 249–250°, and its Ac derivative, m.p. 179–180°]. Comparison of the behaviour towards $C(NO_2)_4$ of (I) and its derivatives with that of chinovaic acid and its derivatives shows that in the triterpene series two CO_2H almost completely inhibit the colour reaction of $C(NO_2)_4$ with double linkings. Methylation of CO_2H completely abolishes this effect. One of the CO_2Me of (II) is hydrolysed to the extent of two thirds by boiling with $N\text{-}KOH\text{-}EtOH$ for 24 hr.; whereas Me₂ chinovate is unchanged by boiling 35% $KOH\text{-}EtOH$. The CO_2Me in ring A of (II) remains unaffected. H. W.

Natural rubber. I. Isolation of the constituents. II. Caoutchene and cautchol and the intermolecular structure of rubber. K. C. ROBERTS (J.C.S., 1938, 215–219, 219–224).—I. A new method of isolating the constituents is described: the primary separation is effected by treating the rubber with a dispersing agent ($COMe_2\text{-}CCl_4$), and the dispersion is further treated with more $COMe_2$. The purely org. non-hydrocarbon constituents are retained in solution on removing the hydrocarbon and the mineral-containing constituents by pptn. Further separation is carried out by selective solvent action. Points established are: (a) rubber hydrocarbon consists of two constituents—caoutchene (I) and cautchol (II)—each of which lacks certain fundamental properties of natural rubber, (b) the existence of two new minor non-hydrocarbon constituents, (c) the separation of the phosphatic material into two contrasted fractions, and (d) the failure to separate completely the major nitrogenous constituent and the rubber hydrocarbon.

II. Crude (I) constitutes 95–98% and (II) 5–2% of rubber hydrocarbon. Pure (I) could not be obtained free from about 1% of nitrogenous matter but appears to be mainly *caoutchene*, $C_{80}H_{128}$. Similarly (II) is mainly *cautchol*, $C_{80}H_{130}(OH)_2$ (*diacetate*), mixed with some acidic material. The influence of (II) on the physical properties of plantation rubber is discussed. Evidence from viscosity measurements and other considerations in support of a two-phase intermol. theory is adduced. F. R. S.

Catalytic polymerisation of ethylenic derivatives. II. Mechanism of dimerisation.

O. SCHMITZ-DUMONT, K. HAMANN, and A. DIEBOLD (Ber., 1938, 71, [B], 205–220; cf. A., 1937, II, 141).—The polymerisation of an ethylenic derivative by acid has been studied in the case of indole (I) since unchanged monomeride can easily be isolated from the polymerised products by distillation with steam. If the solutions are adjusted to the same p_H , polymerisation with $HClO_4$ occurs at the same rate as with HCl . Between H_2SO_4 and H_3PO_4 there is a slight but real divergence ascribed to the fact that the concn. of the acid in a solution of the required p_H is so considerable that the acid is an important part of the solvent. The experiments prove that the polymerisation of (I) by acid is to be regarded in the first place as a H -ion catalysis and since (I) comports itself as an ethylene of the type of $CPh_2\text{:}CH_2$ or indene this conclusion can be extended to the polymerisation of such ethylenes. Support is therefore given to the scheme of Whitmore (Ind. Eng. Chem., 1934, 26, 94) rather than to that of Butlerow and Michael which postulates intermediate ester formation. Examination of the kinetics of the polymerisation of skatole (II) shows that the scheme of Whitmore, whereby in dimerisation by means of acid an active ethylenic mol. reacts with a normal mol. without subsequent migration of H , cannot be here applied. Since (II) behaves as an ethylene of the type of $CPh_2\text{:}CH_2$ or indene, this conclusion may be applied generally to the dimerisation of ethylenes. According to the authors' observations two activated mols. of (II) or of the ethylene invariably react with one

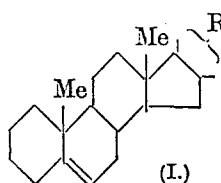
another whereby migration of H takes place as a conclusion of the reaction. Activation of the ethylenic derivative occurs by addition and subsequent elimination of a catalytically active proton. The adducts produced primarily by this addition are not immediately concerned with the process of polymerisation but are essentially the first stage to the activated mols. Catalytic polymerisations by acids and by metallic halides are therefore similar processes. An equilibrium is set up: $A + RHal_n \rightarrow A \cdot RHal_n \rightleftharpoons A^* + RHal_n$. The activated mols. A^* are able to unite to dimeric compounds. In many cases, as with $SnCl_4$ and (I), the primary additive product, $A \cdot RHal_n$, can be isolated. Ability to polymerise is related to the polarity of the ethylenic linking. Some polarity is essential but above a certain limit the tendency towards polymerisation is destroyed. The greater is the polarity and therefore the more strongly the one C is positivised the greater is the proton affinity of the other C and therewith the concn. of the positive group AH^+ in the equilibrium $A + H^+ \rightleftharpoons AH^+ \rightleftharpoons A^* + H^+$. Equally the concn. of the active mols. A^* becomes increased. It is therefore possible that with increasing polarity in the ethylenic linking the ability to polymerise increases. Since, however, dimerisation occurs with migration of H the ability to polymerise depends not only on the polarity but also on the mobility of a definite H atom. With increasing polarity and proton affinity the mobility of the (ultimately) migrating H atom diminishes. This explains why *as*-dianisylethylenes, in contrast to the less strongly positivised *as*-diarylethylenes with smaller polarity in the ethylenic linking, is not dimerised by acids. The possibility of combining an ethylene incapable of polymerisation in consequence of too high polarity with a less polar compound with a mobile H at the ethylenic linking to a "mixed polymeride" has been realised.

H. W.

Lignin and related compounds. XXIX. Acidic hydroxyl groups in spruce lignin. R. G. D. MOORE, G. F. WRIGHT, and H. HIBBERT (Canad. J. Res., 1937, 15, B, 532—535).—That spruce lignin, demethylated with HI (which removes aliphatic OH), contains 0.6 of CO_2H (saponifiable) and 6.9 mol. of aromatic OH, per kg. is shown by methylation with CH_3N_2 and with Me_2SO_4 , and confirmed by treatment with $C_6H_4Me \cdot SO_2Cl$.

A. LI.

Solatubin. III. H. ROCHELMAYER [with E. GEYER and C. S. SHAH] (Ber., 1938, 71, [B], 226—233; cf. A., 1937, II, 80).—The *cis*-position of OH at $C_{(3)}$ to Me at $C_{(10)}$ in solatubin



(I) is established by the formation of a ppt. with digitonin and by the positive result of Zimmermann's hormone reaction. Solatubenone (II) is shown to be an $\alpha\beta$ -unsaturated ketone. Solatubiene contains the two double linkings conjugated and in two rings. During the formation of (II) the double linking migrates from the $\beta\gamma$ to the $\alpha\beta$ position. Reduction of (II) with $Al(OPr^i)_3$ gives a mixture, m.p. 202—203°, $[\alpha]_{D}^{25} + 227.2^\circ$ in $CHCl_3$, of *cis*- Δ^4 -solatubenol, m.p. 203—204°, $[\alpha]_{D}^{25} + 91.5^\circ$ in $CHCl_3$ (acetate, m.p. 181—183°), which gives a strong

positive Rosenheim reaction and is pptd. by digitonin, and *trans*- Δ^4 -solatubenol. All derivatives of (I) hitherto prepared are classified with respect to the position of the double linking and the steric relationships. The relationships are identical with those in the cholestane series. Therefore it may be assumed that the structure of the N-free portion of the mol. of (I) is the same as that of cholesterol.

H. W.

Snake poisons. II. Mode of union of sulphur. K. H. SLOTTA and H. L. FRAENKEL-CONRAT (Ber., 1938, 71, [B], 264—271; cf. A., 1938, III, 335).—The neurotoxin (I) of the highly active freshly-dried but not otherwise purified poison (II) of *Crotalus t. terrificus* is rapidly but not completely destroyed by cysteine at pH 7.6 and room temp.; an equilibrium appears to be reached. Under similar conditions (I) is not affected by cystine. The poison of *Bothrops jararaca* behaves similarly. The action is regarded as due to rupture of the S-S bridge in (I); as with insulin it has not been found possible to re-combine the fragments by dehydrogenation. Treatment of (II) with $NaHSO_3$ causes the appearance of SH groups, the formation of a ppt. with increased S content, displacement of the optical activity towards the negative side, and nullification of the toxic action. The observations are precisely similar to those made by Micheel *et al.* with the venom of *Naja flava* (A., 1937, III, 457) but the explanation offered by these workers is adversely criticised and the change is considered to be due to the production of SH compound and a thiosulphonic acid substance.

H. W.

Constituents of pyrethrum flowers. X. Identification of the fatty acids combined with pyrethrolone. F. ACREE, jun., and F. B. LA FORGE (J. Org. Chem., 1937, 2, 308—313; cf. A., 1935, 1550; 1936, 1514).—Pyrethrin I semicarbazone (I), as prepared from concentrates of light petroleum extracts, is a mixture of the semicarbazones of pyrethrins I and II and of the pyrethrolone esters of unsaturated fatty acids. These acids are separated by saponification of (I) followed by esterification with MeOH. After removal of the Me esters of chrysanthemum-mono- and -di-carboxylic acids, fractionation yields a fraction, b.p. 130—150°/0.5 mm., containing palmitic and linoleic acids. These acids also occur free in the oleo-resins of pyrethrum flowers and are isolated by esterification and fractionation of the light petroleum extracts. Me palmitate and linoleate are separated from the fraction of b.p. 130—150°/0.5 mm.

E. G. B.

Rottlerin. II. K. S. NARANG, J. N. RAY, and B. S. ROY (Current Sci., 1937, 6, 277).—The substance, $C_{19}H_{21}O_6N$ (?), m.p. 206° (cf. A., 1938, II, 66), has been obtained from rottlerin Me_4 ether and $NaNO_2 \cdot AcOH$, and cannot have 19 C. Catalytic reduction ($Pd-H_2$) gives a substance, m.p. 162°, dissolving in alcoholic alkali without giving $PhCHO$; acid ppts. an isomeric substance, m.p. 139°. Substances, m.p. 162° and 139°, resist reduction with PtO_2-H_2 , and substance, m.p. 162°, gives on oxidation ($KMnO_4$) a substance, m.p. 123°.

F. R. S.

Action of iodine on acetylene glycols. A. A. KRUGLOV (J. Gen. Chem. Russ., 1937, 7, 2605—2608).—Glycols of the type $(OH \cdot CRR' \cdot C)_2$ ($R = R' = Ph$;

R = R' = Me; R = Ph, R' = H) react with I in boiling CHCl_3 solution to yield 3 : 4-di-iodo-2 : 2 : 5 : 5-tetraphenyl-, m.p. 213—214°, -2 : 2 : 5 : 5-tetramethyl-, m.p. 109°, or -2 : 5-diphenyl-2 : 5-dihydrofuran, decomp. 146—150°. R. T.

Pyrenium. XXX. Heteropolarity. XXXII. 2-Benzoyl-3 : 4 : 5-triphenylfuran as product of the oxidation of tetraphenylpyrenium salts and of tetraphenylcyclopentadienone. F. QUINT, R. PÜTTER, and W. DILTHEY (Ber., 1938, 71, [B], 356—358).—The product, m.p. 166°, of the oxidation of 2 : 4 : 5 : 6-tetraphenylpyrenium perbromide is identified as 2-benzoyl-3 : 4 : 5-triphenylfuran (I), identical with that derived from tetraphenylcyclopentadienone (A., 1937, II, 463). Fusion of (I) with KOH give BzOH and, probably, 3 : 4 : 5-triphenylfuran, m.p. 137°. H. W.

Geometrical inversion with acids derived from the coumarins. VI. Behaviour of the acids derived from 4-methylcoumarins. K. S. MURTY, P. S. RAO, and T. R. SESHADRI (Proc. Indian Acad. Sci., 1937, 6, A, 316—327).—Long boiling with alkali of 4-methyl- β - and - α -naphthopyrones, 7-hydroxy- (I) and 7-methoxy-4-methylcoumarin (II), and 4 : 7-dimethylcoumarin produces acids which are easily converted into the pyrones by heat or dehydrating agents but do not yield more stable acids by heating with aq. alkali containing HgO, a treatment which converts *cis*- into *trans*-acids (A., 1937, II, 254). They are therefore *trans*-acids, in extension of the ideas of Fries *et al.* (A., 1906, i, 276) but contrary to Dey *et al.* (A., 1932, 1038). This is confirmed by the resistance of their Me ethers to the action of acids or Hg compounds. 4-Hydroxy- β -methylcoumaric acid, m.p. 185°, sinters 115°, cannot be cryst. from boiling EtOH on account of the ease with which it is converted into (I); 4-methoxy- β -methylcoumaric acid, m.p. 145° (decomp.), gives (II) when melted, whilst its Me ether, m.p. 150°, melts without decomp. and is unaffected by *cis* \rightarrow *trans* reagents. Similar stability is shown by β -4-dimethylcoumaric acid Me ether, m.p. 125—126°, and β -1-methoxy-2-naphthylcrotonic acid, m.p. 140°. The ready interconversion of *trans*-acids and pyrones is explained by a tautomeric mechanism (cf. citraconic-mesaconic acids). R. G.

Aluminium chloride, a new reagent for the condensation of β -ketonic esters with phenols. I. Condensations of methyl β -resorcyate, β -resorcylic acid, and resacetophenone with ethyl acetoacetate. S. M. SETHNA, N. M. SHAH, and R. C. SHAH (J.C.S., 1938, 228—232; cf. A., 1937, II, 513).—Me- β -resorcyate (I) and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ (II) with AlCl_3 in PhNO_2 yield Me 5-hydroxy-4-methylcoumarin-6-carboxylate, m.p. 185—186° (acetate, m.p. 153—155°; benzoate, m.p. 164—166°; Me ether, m.p. 106—107°), hydrolysed (HCl) to 5-hydroxy-4-methylcoumarin-6-carboxylic acid, m.p. 244° [also formed from β -resorcylic acid, (II), AlCl_3 , and PhNO_2], and decarboxylated by aq. HCl-AcOH at 180° to 5-hydroxy-4-methylcoumarin (benzoate, m.p. 175—177°), which with NaOH and Me_2SO_4 yields 2 : 6-dimethoxy- β -methylcinnamic acid, m.p. 148—150°. (I), (II), and ZnCl_2 at 135—140° give (mainly) Me 7-hydroxy-4-methylcoumarin-6-carboxylate and a

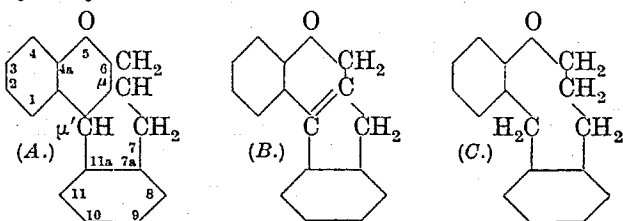
little of the 5-OH-derivative. Resacetophenone, (II), and AlCl_3 in PhNO_2 give 5-hydroxy-6-acetyl-4-methylcoumarin (III), m.p. 165° [acetate, m.p. 152°; phenylhydrazone, m.p. 236—237°; oxime, m.p. 260° (decomp.); semicarbazone, m.p. 290° (decomp.)]. (III) with Ac_2O -NaOAc at 150—160° yields 3'-acetyl-4 : 2'-dimethylchromono-7' : 8' : 6 : 5- α -pyrone, m.p. 204°, and with Bz_2O and NaOBz at 180—190° yields 3'-benzoyl-2'-phenyl-4-methylchromono-7' : 8' : 6 : 5- α -pyrone, m.p. 301°, whilst Clemmensen reduction of (III) gives 5-hydroxy-4-methyl-6-ethylcoumarin, m.p. 174—175°. (III) is also obtained from 5-acetoxy-4-methylcoumarin and AlCl_3 at 170—180°. J. D. R.

Optically active flavanones. III. Asymmetric synthesis of hydroxyflavanone from hydroxychalkone. S. FUJISE and H. SASAKI (Ber., 1938, 71, [B], 341—344; cf. A., 1936, 1263).—*l*-Matteucinol is racemised by aq.-alcoholic KOH slowly at room temp., more rapidly when heated, the effect being due apparently to intermediate wandering of H to C:O. Ac_2O containing a little conc. H_2SO_4 and (I) give *l*-matteucinol diacetate [4'-methoxy-5 : 7-diacetoxy-6 : 8-dimethylflavanone], m.p. 169.5—170°, $[\alpha]_D^{25} +32.7^\circ$ in dioxan; the corresponding *dl*-compound has m.p. 172—172.5°. Boiling Ac_2O and NaOAc transform (I) into 2' : 4' : 6'-triaceoxy-3 : 5'-dimethylphenyl 4-methoxystyryl ketone, m.p. 152—153°; this passes when heated at 100° with EtOH containing *d*-camphorsulphonic acid into *d*-matteucinol diacetate, m.p. 173—173.5°, $[\alpha]_D^{25} +32.1^\circ$ in dioxan. H. W.

Natural coumarins. XXXVI. Occurrence of seselin in Japanese *Skimmia* species. E. SPÄTH and O. NEUFELD (Ber., 1938, 71, [B], 353—356).—Extraction of the leaves of *S. japonica*, Thbg., with Et_2O leads to seselin, $\text{C}_{14}\text{H}_{12}\text{O}_3$, m.p. 119—120°, identical with the substance obtained by Bose and Guha from *Seseli indicum*; both compounds are hydrogenated (Pd-sponge in AcOH) to tetrahydro-seselin, m.p. 106—107°. It is also probably identical with the material obtained by Asahina from *S. japonica*, Thbg., and *S. repens*, Nakai (A., 1930, 967, 1454).

dl-6 : 7-Dimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline has m.p. 53—53.5°. H. W.

Dimethoxychromindene. P. PFEIFFER and E. DÖRING (Ber., 1938, 71, [B], 279—284).—It is proposed to designate the systems A, B, and C chromindane, chromindene, and lyochromindane, respectively. Brasilin is thus 3 : 9 : 10 : μ -tetrahydroxy- and hæmatoxylin is 3 : 4 : 9 : 10 : μ -penta-hydroxy-chromindane.



Passage of HCl into a solution of chromanone (I) and vanillin Me ether in abs. EtOH and treatment of the

product with H_2O gives 3':4'-dimethoxybenzylidene-chromanone, m.p. 123.5—124.5°, reduced (Pd-BaSO₄ in AcOH) to 3':4'-dimethoxybenzylchromanone, m.p. 88.5—89.5°. This is cyclised by P_2O_5 in boiling C_6H_6 to 9:10-dimethoxychromindene, m.p. 177—179.5°, transformed by anhyd. FeCl₃ in boiling AcOH into the salt, $[C_{18}H_{15}O_3](FeCl_4)$, which darkens at 180° and becomes resinified at 200°. $m-OH \cdot C_6H_4 \cdot CHO$ and (I) yield 3'-hydroxybenzylidenechromanone, m.p. 201° (acetate, m.p. 103—104°, which gives only non-cryst. products when hydrogenated). 3'-Methoxybenzylidenechromanone, m.p. 89—90° (hydrochloride, m.p. 103—104°), is hydrogenated (Pd-BaSO₄ in AcOH) to 3'-methoxybenzylchromanone, m.p. 58—59°; this is mainly unaffected by P_2O_5 in boiling C_6H_6 but becomes resinified in boiling PhMe. H. W.

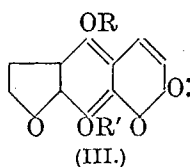
Recent developments in the chemistry of the catechins. K. FREUDENBERG (Stiasny Festschr., 1937, 53—54).—The dispute over the formula for catechin is ended because P. Maitland has isolated pentamethylepicatechin from the reduction products of pentamethylquercetin and Nierenstein accepts this as establishing the Freudenberg formula. D. B.

New rhodamine dye from *p*-cymene. P. KIRJAKKA and N. ÄÄRI (Suomen Kem., 1938, 11, B, 1).—1:4:2- $C_6H_3MePr^tNH_2$ and $m-C_6H_4(OH)_2$ in presence of H_3BO_3 give 3-hydroxy-2'-methyl-5'-isopropylidiphenylamine, m.p. 55°, b.p. 233—234°/14 mm. which with $o-C_6H_4(CO)_2O$ gives NN'-di-(2-cymyl)rhodamine, which dyes wool blue-violet.

M. H. M. A.

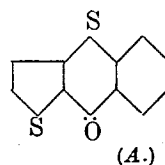
Chemical constituents of Umbelliferae. V. Constituents of the root of *Angelica glabra*, Makino. I. T. NOGUCHI and M. KAWANAMI (Ber., 1938, 71, [B], 344—352).—Prolonged extraction of the roots with Et_2O gives *byak-angelicol*, m.p. 106°, $[\alpha]_D^{25} +34.77^\circ$ in C_5H_5N , and *byak-angelicin* (I), m.p. 125—126°, or $(+1H_2O)$ m.p. 117—118°, $[\alpha]_D^{25} +24.62^\circ$ in C_5H_5N (name based on that of the Japanese drug "Byakusi"). Analyses and determinations of mol. wt. show (I) to be $C_{17}H_{18}O_7$. It contains 1 OMe and 2 OH (diacetate, m.p. 118—119°) but does not react with the customary carbonyl reagents. It contains a lactone group. The penultimate O of (I) is present in a furan ring since (I) is oxidised by H_2O_2 to furan-2:3-dicarboxylic acid. The presence of a reactive double linking in (I) is established by reduction with Na-Hg in alkaline solution to the *hydroxydihydro-acid* (II), $C_{17}H_{22}O_8$, m.p. 141°, also obtained by hydrogenation (Pt-sponge in AcOH) and converted by distillation/1 mm. into *dihydro-byak-angelicin*, $C_{17}H_{20}O_7$, m.p. 120—122°, also obtained by methylation of (II). Oxidation of (II) with HNO_3 (d 1.4) gives succinic acid, which is not derived similarly from (I). The ultimate O of (I) is in an ether linking since treatment of (I) with AcOH containing a trace of H_2SO_4 gives 5-hydroxy-8-methoxy- or 8-hydroxy-5-methoxy-2':3'-7:6-furocoumarin, m.p. 212° (monoacetate, m.p. 180°), methylated by CH_3N_2 to isopimpinellin, thus establishing the fundamental skeleton of (I). The composition of the residue $C_5H_{11}O_2$ coincides with that of oxypeucedanine hydrate. Oxidation of (I) with CrO_3 in AcOH affords $COMe_2$ and a quinone, decomp. 250°, identical with bergapten-

quinone or xanthotoxinquinone [bergaptenquinol, m.p. 275° (decomp.) (also *dihydrate*), and its *diacetate*, m.p. 210°] and *byak-angelic acid* [(III), $R = CH_2 \cdot CO_2H$ and $R' = Me$ or $R = Me$ and $R' = CH_2 \cdot CO_2H$], m.p. 227° (*Me ester*, m.p. 167°), whereas treatment with $KMnO_4$ leads to $OH \cdot CMe_2 \cdot CO_2H$. Further (I) when heated with P_2O_5 in PhMe affords *anhydrobyak-angelicin* [(III) $R = CH_2 \cdot COPr$ and $R' = Me$ or $R = Me$ and $R' = CH_2 \cdot COPr^t$], m.p. 107° (*oxime*, m.p. 183—186°; *semi-carbazone*, m.p. 182°), oxidised by H_2O_2 in presence of alkali to Pr^tCO_2H . (I) is therefore (III) with $R = CH_2 \cdot CH(OH) \cdot CMe_2 \cdot OH$ and $R' = Me$ or $R = Me$ and $R' = CH_2 \cdot CH(OH) \cdot CMe_2 \cdot OH$. H. W.



Stereoisomeric forms of tetrahydrothiophen-2:5-dicarboxylic acid. A. FREDGA (J. pr. Chem., 1938, [ii], 150, 124—132).—dl- $(CH_2 \cdot CHBr \cdot CO_2Na)_2$ (I) and aq. Na_2S give (trans)-dl-tetrahydrothiophen-2:5-dicarboxylic acid (II), m.p. 165—166°, $k 5 \times 10^{-4}$, giving the l- (*brucine salt*) and d-form (III) (*quinine salt*), m.p. 179—180°, $[\alpha]_D^{25} 225.3$ in 0.4N-HCl. The (cis)-meso-acid, m.p. 144—145°, $k 4.6 \times 10^{-4}$, is similarly obtained. Mixed m.p. curves are given for the active acids and their Se analogues and for (III) and the l-Se-analogue which form a 1:1 additive compound, m.p. 177°. K_2S_2 and (I) give tetramethylene disulphide $\alpha\delta$ -dicarboxylic acid, m.p. about 270° (decomp.), and (II). The meso-acid and K_2S_2 give an inseparable mixture. R. S. C.

Thiophen series. XLI. Derivatives of 3-iodothiophen. W. STEINKOPF and H. F. SCHMITT (Annalen, 1938, 533, 264—269).—Conversion of tetraiodothiophen into 3-iodothiophen (I) is better effected with Al filings than with Al powder. The direct Grignard reaction of (I) is impossible but the desired compound (II) is obtained when (I) and EtBr in Et_2O are treated with Mg; addition of $CH(OEt)_3$ to the product gives *thiophen-3-aldehyde*, b.p. 78°/14 mm. (*phenylhydrazine*, m.p. 138—139°; *oxime*, m.p. 111—112°), which rapidly darkens on exposure to air. Treatment of (II) with CO_2 at 0° affords *thiophen-3-carboxylic acid*, m.p. 137—138°, converted by boiling $SOCl_2$ into the corresponding *chloride*, m.p. 53—54°, and by Ac_2O in boiling PhMe into the *anhydride*, b.p. 213°/12 mm., m.p. 54.5—56°. Dry distillation of *Ca thiophen-3-carboxylate* affords 3:3'-*dithienyl ketone*, m.p. 72—73°, in very small yield. $o-SH \cdot C_6H_4 \cdot CO_2H$, (I), anhyd. K_2CO_3 , and $Cu(OAc)_2$ in amyl alcohol at 135—140° give *o-3'-thienylthiobenzoic acid* (II), m.p. 191° after softening at 187°, transformed by fuming HNO_3 into *o-2'-nitro-3'-thienylsulphoxido-benzoic acid*, decomp. 237.5° after darkening at about 210°, which is not affected by conc. H_2SO_4 at 95—100°. At 90° conc. H_2SO_4 converts (II) into 2':3'-*thiophenothiochromone* (A), m.p. 161.5°, the constitution of which is deduced from its colour, its colorimetric behaviour with conc. H_2SO_4 , and the greater reactivity of the α -atoms. *o-2'-Thienylthiobenzoic acid* is transformed by fuming HNO_3 at 40—



50° into *o*-3':5'-dinitro-2'-thienylsulphoxidobenzoic acid, decomp. 217.5°. H. W.

Thiophen seires. XLII. Reactions of 3:4-dibromothiophen-2:5-dialdehyde. W. STEINKOPF and N. EGER (Annalen, 1938, 533, 270—278).—3:4-Dibromothiophen-2:5-dialdehyde (I) is transformed by 50% KOH without cooling into 3:4-dibromothiophen (II), b.p. about 210° (identified as 3:4-dibromo-2-nitrothiophen, m.p. 115—116°), 3:4-dibromo-2-thienyl alcohol (III), m.p. 84° (identified by conversion into 3:4-dibromo-2-thienyl bromide, m.p. 57°), and 3:4-dibromo-2-thiophenic acid (IV). In an individual experiment 3':4'-dibromo-2'-thienyl 3:4-dibromo-2-thiophenate, m.p. 115°, was obtained; since this gives (II), (III), and (IV) with HCO₂H when hydrolysed it must be regarded as a normal intermediate. With 50% KOH at >20° (I) yields (III), 3:4-dibromo-2:5-dihydroxymethylthiophen, m.p. 174°, (IV), 3:4-dibromo-5-hydroxymethyl-2-thiophenic acid, m.p. 229°, and 3:4-dibromothiophen-2:5-dicarboxylic acid, m.p. 321°. The behaviour of (I) is therefore intermediate between that observed by Lock for aromatic aldehydes in which both positions *ortho* to CHO are occupied by halogen and those in which only one position is thus occupied. The course of the reaction between (I) and N₂H₄.H₂O depends greatly on conditions. In hot AcOH the carmine-red, completely insol., infusible 3:4-dibromothiophen-2:5-dialdehydediazine (A) results. In hot C₅H₅N small



amounts of the unstable 3:4-dibromothiophen-2:5-dialdehydedemonazinedihydrazone (B) (R = N-NH₂) result, with larger quantities of the dihydrazone. With a large excess of (I) in C₅H₅N the infusible monazine (B; R = O) is obtained.

p-C₆H₄(CHO)₂ and excess of N₂H₄.H₂O in a freezing mixture give terephthalaldehydedihydrazone (V), m.p. 169°. In AcOH the product is terephthalaldehydediazine, N:CH.C₆H₄.CH:N, also obtained from (V) and *p*-C₆H₄(CHO)₂ and, best, by heating (V) at 150° and then at 200°. *m*-C₆H₄(CHO)₂ and N₂H₄.H₂O similarly give isophthalaldehydedihydrazone, m.p. 115°, converted by *m*-C₆H₄(CHO)₂ into isophthalaldehydediazine.

H. W.

Thermal decomposition of unsaturated quaternary salts. R. LUKEŠ (Coll. Czech. Chem. Comm., 1938, 10, 66—76).—1:1-Dimethyl-2-methylene-pyrrolidinium (I), NPhMe₃, 1-methylpyridinium, and homoneurine formates at 200° give respectively 1:2-dimethylpyrrolidine, NPhMe₂, 1-methylpiperidine (cf. Mayo, A., 1937, II, 208), a mixture of dimethylallylamine and NMe₃, together with Me and allyl formates. The acetate of (I) at 200° yields 1:2-dimethyl-Δ²-pyrroline. F. R. G.

Selective hydrogenation of substituted amides. J. C. SAUER and H. ADKINS (J. Amer. Chem. Soc., 1938, 60, 402—406).—When hydroxymethyl-, carb-

ethoxy-, or carbamyl derivatives of cyclic amides are hydrogenated at 200—260°/200—300 atm. in the presence of Cu-Cr oxide, the position attacked depends on the nature of the ring and the substituent and the position of the latter. 5-Carboethoxy-2-pyrrolidone (prep. from glutamic acid), b.p. 157°/4 mm., gives 93% of 5-hydroxymethyl-2-pyrrolidone, m.p. 87°, b.p. 185—187°/4 mm. (3:5-dinitrobenzoate, m.p. 109—110°). 2-Pyrrolidone-5-carboxy-*n*-amylamide, m.p. 110—111°, gives 68% of 5-*n*-amylaminomethyl-2-pyrrolidone, b.p. 156—158°/1 mm. (hydrochloride, m.p. 181—185°), with 25% of 5-hydroxymethyl- plus 2-amylaminomethylene-pyrrolidine. *Et* 5-methyl-1-*n*-amyl-2:3-dihydropyrrolone-4-carboxylate (from C₅H₁₁.NH₂, *Et* acetosuccinate, and *Et*OH at room temp.), m.p. 60—61°, b.p. 138—140°/1 mm., gives 60% of 5-methyl-4-hydroxymethyl-1-*n*-amyl-2-pyrrolidone, b.p. 176°/2 mm. (phenylurethane, m.p. 73°), 15% of *Et* 5-methyl-1-*n*-amyl-2-pyrrolidone-4-carboxylate, b.p. 153°/3 mm., and 15% of 2-methyl-3-hydroxymethyl-1-*n*-amylpyrrolidine, b.p. 76—78°/12 mm.; similarly *Et* 1-β-phenylethyl-5-methyl-2-pyrrolidone-4-carboxylate, b.p. 167°/1 mm., m.p. 67°, gives 55% of 1-β-phenylethyl-5-methyl-4-hydroxymethyl-2-pyrrolidone, b.p. 180—183°/1 mm. (3:5-dinitrobenzoate, m.p. 141—142°), and 13% of 1-β-phenylethyl-2:3-dimethylpyrrolidine, b.p. 73—75°/2 mm. (hydrochloride, m.p. 190—192°). *Et* 6-methyl-1-*n*-amyl-2-piperidone-5-carboxylate, b.p. 127°/1 mm., gives 49% of 6-methyl-5-hydroxymethyl-1-*n*-amyl-2-piperidone, b.p. 156°/1 mm. (phenylurethane, m.p. 103°), and 30% of 2:3-dimethyl-*n*-amylpiperidine, b.p. 93—95°/9 mm. (hydrochloride, m.p. 148—151°). 1-*n*-Amyl-2-piperidone-5-carboxy-*n*-amylamide, b.p. 200°/1 mm., m.p. 102°, gives 60% of 1-*n*-amylpiperidine-3-carboxy-*n*-amylamide, b.p. 141—144°/1 mm. (*p*-toluenesulphonate, m.p. 147—148°), 31% of 1-*n*-amyl-3-hydroxymethylpiperidine, b.p. 89—90°/1 mm. (hydrochloride, m.p. 188—191°), and 6% of 1-*n*-amyl-3-*n*-amylaminomethylpiperidine, b.p. 67°/8 mm. (hydrochloride, m.p. 184—186°). *Et* 2-keto-1:2-dihydroquinoline-4-carboxylate [from isatin and CH₂(CO₂H)₂], m.p. 202—203°, gives first the H₄-ester, m.p. 134—135° [also obtained from *o*-NO₂.C₆H₄.CH₂C(CO₂Et)₂ and H₂-Raney Ni in dioxan], then 2-keto-4-hydroxymethyl-1:2:3:4-tetrahydroquinoline, b.p. 172—175°/8 mm. (3:5-dinitrobenzoate, m.p. 134—136°), and finally 4-methyl-1:2:3:4-tetrahydroquinoline, b.p. 110°/8 mm. (Bz derivative, m.p. 138°; the sole product if hydrogenation is prolonged). *Et* 2-keto-1:2:3:4-tetrahydroquinoline-4-carboxylate loses its CO₂Et, giving first 2-keto-1:2:3:4-tetrahydroquinoline and then 1:2:3:4-tetrahydroquinoline, which is the sole product (85%) of prolonged reduction. *Et* γ-N-piperidinobutyrate, b.p. 108°/1 mm., gives only δ-N-piperidinobutyl alcohol and butane-α,δ-diol; similarly *Et* ε-N-piperidinoheptanoate, b.p. 134—136°/1 mm., gives only hexane-α,ε-diol and *Et* ζ-N-piperidinoheptanoate, b.p. 127—128°/8 mm. (3:5-dinitrobenzoate, m.p. 171—172°). C₅H₁₁.NH₂, *Et* α-acetoglutarate, and *Et*OH give *Et* 6-methyl-1-*n*-amyl-1:2:3:4-tetrahydro-2-pyridone, b.p. 130°/1 mm., reduced by H₂-Raney Ni at 120—125° to the piperidone. *Et* 1-β-phenylethyl-5-methyl-2:3-dihydropyrrolone-4-carb-

oxylate, b.p. 170°/1 mm., m.p. 77°, is obtained from $\text{Ph}[\text{CH}_2]_2\text{NH}_2$ and Et acetosuccinate and is reduced (Raney Ni) to the pyrrolidone. R. S. C.

3:4-Dimethylpyrrole and its derivatives. H. FISCHER and H. HÖFELMANN (Annalen, 1938, 533, 216—230).—Reduction (Raney Ni at 150—160°) of Et 3-aldehydo-2:4-dimethylpyrrole-5-carboxylate (I) gives Et 2:3:4-trimethylpyrrole-5-carboxylate (II), m.p. 128°, in good yield accompanied particularly if (I) is not pure by Et₂ 2:2':4:4'-tetramethyl-3:3'-dipyrrolylmethane-5:5'-dicarboxylate, m.p. 228°. With SO_2Cl_2 in Et₂O (II) gives a variety of products by reason of the sensitiveness of the Cl-substance towards acids and heat. Compounds, $\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$, m.p. 73°, Et₂ 3:4-dimethylpyrrole-2:5-dicarboxylate, and products, m.p. 235° (decomp.) and m.p. 177°, respectively, are thus obtained; under defined conditions Et 5-carboxy-3:4-dimethylpyrrole-2-carboxylate is obtained in good yield and reasonably free from by-products. It is decarboxylated at 250° to Et 3:4-dimethylpyrrole-2-carboxylate (III), b.p. 120—125°/11 mm., m.p. 96°, which with 40% KOH gives 3:4-dimethylpyrrole (IV) in 85% yield. Successive additions of (IV) and AcBr to MgEtBr in Et₂O yield 2-acetyl-3:4-dimethylpyrrole, m.p. 135°, brominated in AcOH to the compound, $\text{C}_8\text{H}_9\text{ONBr}$, decomp. 180°, which when crystallised from dil. EtOH, dil. COMe_2 , or AcOH affords the substance, $\text{C}_8\text{H}_{10}\text{ONBr}$, m.p. 105°. HCN, HCl, and (IV) in abs. Et₂O yield the aldimine hydrochloride, $\text{C}_8\text{H}_{11}\text{N}_2\text{Cl}$, decomp. 240°, which with boiling H_2O gives 3:4-dimethylpyrrole-2-aldehyde (V), m.p. 133°, converted by Br in AcOH into 2-bromo-3:4-dimethylpyrrole-5-aldehyde, m.p. 185°. Attempts to introduce a second CHO group into (IV) directly by HCl-HCN or according to Tiemann-Reimer were unsuccessful. Therefore (V) is condensed with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ or $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ to Me (VI), m.p. 190—191°, and Et, m.p. 156°, 3:4-dimethylpyrrole-2-cyanoacrylate, $\text{CMe}\cdot\text{CMe}\cdot\text{CH}=\text{NH}\cdot\text{CH}=\text{C}(\text{CN})\cdot\text{CO}_2\text{R}$. Similarly condensation with $\text{CH}_2(\text{CN})_2$ gives the product, $\text{C}_{10}\text{H}_9\text{N}_3$, m.p. 225° after softening. Treatment of (VI) in $\text{CHCl}_3\text{-Et}_2\text{O}$ with HCl-HCN yields Me 2-aldehydo-3:4-dimethylpyrrole-5-cyanoacrylate, m.p. 168° after softening; the corresponding Et ester has m.p. 130° after softening. Treatment of these esters with KOH-EtOH- H_2O at 100° leads to 3:4-dimethylpyrrole-2:5-dialdehyde, m.p. 158°. (III) is converted by Br in AcOH into Et 2-bromo-3:4-dimethylpyrrole-5-carboxylate, m.p. 134°, and is hydrolysed by NaOH to 3:4-dimethylpyrrole-2-carboxylic acid, m.p. 235° (decomp.) when rapidly heated. Treatment of (III) with MgEtBr and AcBr in Et₂O or with AcCl and AlCl_3 in CS_2 yields Et 2-acetyl-3:4-dimethylpyrrole-5-carboxylate, m.p. 106°. Hydrogenation (Ni at 150—160° under pressure) of Et 3-aldehydo-4-methyl-2-ethylpyrrole-5-carboxylate gives Et 3:4-dimethyl-2-ethylpyrrole-5-carboxylate, b.p. 158°/11 mm., m.p. 78°, accompanied by Et₂ 4:4'-dimethyl-2:2'-diethylpyrromethane-5:5'-dicarboxylate, m.p. 211°. 3:4-Dimethyl-2-ethylpyrrole-5-carboxylic acid, m.p. 143° (decomp.), is decarboxylated at 140—145° to 3:4-dimethyl-2-ethylpyrrole, b.p. 84°/11 mm., which with

boiling AcOH-Ac₂O affords 5-acetyl-3:4-dimethyl-2-ethylpyrrole, m.p. 123°. II. W.

Indole formation from pyrroles. C. F. H. ALLEN, D. M. YOUNG, and M. R. GILBERT (J. Org. Chem., 1937, 2, 235—244).—The indole prepared from acetone-*m*-tolylhydrazine and shown by Plancher (A., 1907, i, 80) to be identical with that prepared by Dennstedt from the dipyrrole derived from 2-methylpyrrole (I) is 2:4-dimethylindole (II), being different from 2:5- (III) (cf. lit.), 2:6-, m.p. 86° (picrate, m.p. 132°), and 2:7-, m.p. 35°, b.p. 129—131°/2 mm. (picrate, m.p. 149°), -dimethylindole. Plancher's mechanism (*loc. cit.*) for indole formation from dipyrroles involves dissociation of the latter and hydrolysis of one mol. of pyrrole to NH_3 and a 1:4-diketo-compound, which condenses with another mol. of pyrrole. Dimethyldipyrrole (IV) when treated with acid rapidly gives the indole, obtained only after prolonged heating of (I) with acid; no dissociation of (IV) to (I) was detected. Dipyrrole is therefore a probable intermediate in indole formation from pyrroles. Acid hydrolysis of a series of pyrroles failed to show the formation of 1:4-diketo-compounds, except from (III) (cf. A., 1934, 1109). Moreover, (I) when heated with AcOH-Zn(OAc)₂ in presence or absence of 2:4-dinitrophenylhydrazine gives (II). With pyrrole some 2-acetylpyrrole is formed but no reaction occurred with 2-phenyl- and 2-acetylpyrrole. The following were obtained from the appropriate pyrrole by heating with acetonylacetone and Zn(OAc)₂-AcOH: 2:4:7-trimethyl-, 3-carboxy-2:4:7-trimethyl-, and 2-phenyl-4:7-dimethyl- (picrate, m.p. 171—172°) -indole. The last was also obtained from phenacyl-*p*-xylylide by Bischler's method. Similarly, 2:4-, m.p. 209°, and 2:5-, m.p. 192—193°, -diphenylindole were prepared; neither forms a picrate. Phenacyl-*m*-xenylamine has m.p. 134°, whilst the *p*-isomeride has m.p. 148° (picrate, m.p. 130—131°); the picrates of *o*-, *m*-, and *p*-xenylamine have m.p. 163—164°, 196°, and 198—199°, respectively. These results confirm the structure assigned to the dipyrroles (Allen *et al.*, A., 1938, II, 158), but are not in accord with Plancher's mechanism for indole formation. A new mechanism similar to a "diene" synthesis with subsequent elimination of NH_3 is proposed.

H. G. M.

Indole formation from pyrroles. Addendum and correction. C. F. H. ALLEN (J. Org. Chem., 1937, 2, 400; cf. preceding abstract).—2:4-Dimethylindole, synthesised from acet-*o*-3-xylylide, is identical with the product obtained by acid treatment of 2-methylpyrrole and of the corresponding dipyrrole.

E. G. B.

Nitrogenous heterocyclic rings. XXXIV. Reduction of isatogens. III. Reduction of 2-phenylisatogen. P. RUGGLI, H. ZAESLIN, and R. GRAND (Helv. Chim. Acta, 1938, 21, 33—37).—2-Phenylisatogen (I), best prepared by protracted insolation of the variety of higher m.p. of *o*-nitrostilbene dichloride in $\text{C}_6\text{H}_5\text{N}$, absorbs 4 H in presence of Raney Ni in EtOAc and gives 2-phenylindoxyl, isolated as its Ac derivative, m.p. 108°. The hydrogenated solution (without being acetylated) on exposure to air gives yellow crystals of the compound

(II), $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown NH \end{smallmatrix} CPh \cdot O \cdot C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown CPh \end{smallmatrix} NH$ (Angeli and Angelico, A., 1907, i, 153; Kalb and Bayer, A., 1912, i, 726). Hydrogenation of (I) with 2 H does not afford homogeneous phenylindolone but (II). Reduction with a little $NHPh \cdot NH_2$ in C_5H_5N proceeds similarly.

H. W.

Amine oxides of the isoquinoline and isoindole series. P. PFEIFFER and E. MILZ (J. pr. Chem., 1938, [ii], 150, 133—139).—The autoxidation product, $C_{23}H_{20}O_3N_2$, m.p. 214.5°, of 3-phenylindan-3-one-2-p-dimethylaminoanil absorbs 1 O in boiling Ac_2O to give the *amine oxide* (I), m.p. 201°. 3-Phenyl-2-p-dimethylaminophenyldihydroisoindol-1-one (prep. from $o\text{-}CO_2H \cdot C_6H_4 \cdot COPh$ and $p\text{-}NMe_2 \cdot C_6H_4 \cdot NH_2$) similarly absorbs 1 O to give the *amine oxide*, m.p. 198°, also obtained with CO by warming (I) in conc. H_2SO_4 and giving HCO_2H and 3-phenyl-2-p-methylaminodihydroisoindol-1-one, m.p. 178° (*Ac* derivative, m.p. 201—202°), when heated alone at 120°. With $HCl \cdot AcOH$ (I) gives α -phenylphthalide. R. S. C.

Quaternary pyridinium compounds. C. ROHMANN and K. ZIETAN (Ber., 1938, 71, [B], 296—302).— C_5H_5N and $(CH_2I \cdot CH_2)_2O$ in boiling $EtOH$ yield *di- β -1-iodo-1-pyridylethyl ether* (I), $(C_5H_5NI \cdot CH_2 \cdot CH_2)_2O$, m.p. 108—109°, converted by Ag_2O in H_2O into *di- β -1-hydroxy-1-pyridylethyl ether* (II), characterised as the corresponding *platinichloride*, m.p. 246—247° (decomp.), and *dipicrolonate*, m.p. 195°. Oxidation of (I) by $K_3Fe(CN)_6$ in alkaline solution at room temp. gives *di-2-pyridonylethyl ether* ($O \cdot C_5H_4N \cdot CH_2 \cdot CH_2)_2O$, m.p. 158° (*dipicrolonate*, m.p. 258°). 2-Methylpyridine and $(CH_2I \cdot CH_2)_2O$ afford *di- β -1-iodo-2-methyl-1-pyridylethyl ether* (II), m.p. 166—167° (*dipicrolonate*, m.p. 197°). Similarly 3-methylpyridine gives *di- β -1-iodo-3-methyl-1-pyridylethyl ether* (III), m.p. 188—190° [*dipicrolonate*, m.p. 198° (incipient decomp.)]. Pyridine-3-carboxyldiethylamide (IV) yields *di- β -1-iodo-3-diethylcarbamyl-1-pyridylethyl ether* (V), m.p. 135° [*dipicrolonate*, m.p. 264—266° (decomp.)]. The relative surface tensions of solutions of (I), (II), and (III) in H_2O differ little from that of an equally conc. solution of KI whereas that of (V) is < that of (IV). Curare action on frogs is shown by (I), (II), and (III), but not, in accordance with the surface tension, by (V).

H. W.

Quinoline series. II. Syntheses of cinchonic acid. E. THIELEPAPE (Ber., 1938, 71, [B], 387—400).—Successive addition of $Et_2C_2O_4$ and $NPhMeAc$ to $NaOEt$ in Et_2O yields *ethoxalyl-N-methylacetanilide*, $NPhMe \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et$, m.p. 84.5° (corr.) [*Cu* salt, m.p. 205—206° (corr.)], converted by conc. H_2SO_4 at >0° into *Et 1-methyl-2-quinolone-4-carboxylate*, m.p. 134—135° (corr.), hydrolysed to 1-methyl-2-quinolone-4-carboxylic acid, m.p. 250° (corr.). The ester is transformed by PCl_5 in $POCl_3$ at 75—80° and then at 110—112° into *Et 2-chloroquinoline-4-carboxylate* (I), m.p. 63° (corr.), hydrolysed by $NaOH$ to 2-chloroquinoline-4-carboxylic acid, m.p. indef. 230—250° after becoming yellow at 192° (corr.) and softening at 198—200° (corr.), and converted by boiling 30% $NaOH$ into 2-hydroxyquinoline-4-carboxylic acid, m.p. 343° (corr.) [*Et* ester (II), m.p. 209° (corr.)], the monohydrated form of which is probably o-

aminophenylfumaric acid. With KI , red P, and HI (*d* 1.7 or 1.5) (I) yields 2-iodoquinoline-4-carboxylic acid (III), m.p. 184° (corr.) [*Na* salt (+8 H_2O), m.p. 290—315° (corr.) after softening and becoming yellow at about 240° (corr.)]. Conc. HCl and $SnCl_2$ at 100° convert (I) into cinchonic acid (IV), m.p. 256° (corr.) [double salt, $(C_{10}H_7O_2N \cdot HCl)_2 \cdot SnCl_4$, m.p. 266—267° (corr.; decomp.)]; *Cu* salt, m.p. 299° (corr.; decomp.) when not too slowly heated; *aurichloride*, m.p. 252° (decomp.); *picrate*, m.p. 226—227° (decomp.); *hydrazide*, m.p. 154° (corr.); *Et* ester, b.p. 173° (corr.)/10 mm.]. Reduction of (I) with red P and HI (*d* 1.70) gives (IV) and 2-*keto*-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, m.p. 219—220° (corr.) [*Me*, m.p. 164° (corr.), and *Et*, m.p. 157—158° (corr., esters)], the monohydrate of which is probably o-aminophenylsuccinic acid. Catalytic reduction (Pt-sponge in H_2O) of (III) gives (IV) in very good yield. Addition of the condensation product from $NHPhAc$ and $Et_2C_2O_4$ to conc. H_2SO_4 affords (II) in small amount.

H. W.

Relationship between β -naphthylamine and ethyl β -aminocrotonate. J. KENNER, W. H. RITCHIE, and R. L. WAIN (J.C.S., 1937, 1526—1529).—Condensation of 2-hydroxymethylcyclohexanone (I) with $\beta\text{-}C_{10}H_7 \cdot NH_2$ (cf. A., 1907, i, 842) affords a mixture of *tetrahydro- β -naphthacridine*, m.p. 94—94.5° (*picrate*, m.p. 253—254°), dehydrogenated to β -naphthacridine, m.p. 106° [*picrate*, m.p. 247—248° (decomp.); cf. lit.], and an isomeric *H₄-base*, m.p. 114—115° [*picrate*, m.p. 218—219° (decomp.)], dehydrogenated to β -naphthaphenanthridine, m.p. 127° [*picrate*, m.p. 266—267° (decomp.)]. The same products were obtained using 1 : 2- $C_{10}H_6Br \cdot NH_2$. Similarly (I), 3 : 2- $C_{10}H_6Br \cdot NH_2$ (II), its hydrochloride, hydrated $SnCl_4$, and $EtOH$ give two isomeric *bromotetrahydro-bases*, $C_{17}H_{14}NBr$, m.p. 133° and m.p. 145° [*picrates*, m.p. 206° (decomp.) and m.p. 156—157° (decomp.), respectively]. Condensation of (I) with *Et* β -aminocrotonate (III) gives *Et dihydrolutidinedicarboxylate* and *Et 2-methyl-1 : 4 : 5 : 6 : 7 : 8-hexahydroquinoline-3-carboxylate*, b.p. 171—174.5°/18 mm. (*picrolonate*, m.p. 212—214°), dehydrogenated by Se (320°, 18 hr.) to 2-methylquinoline (*picrolonate*, m.p. 231—232.5°), and hydrolysed by boiling HCl (*d* 1.17) to 2-methyl-5 : 6 : 7 : 8-tetrahydroquinoline-3-carboxylic acid (A., 1934, 1111). This when distilled with $NaOH \cdot CaO$ gives 2-methyl-5 : 6 : 7 : 8-tetrahydroquinoline (*picrolonate*, m.p. 220°). $\beta\text{-}C_{10}H_7 \cdot NH_2$ is intermediate in character between (III) and other aromatic amines already studied. Details for the prep. of the following are described (cf. Wynne, Proc. C.S., 1914, 30, 204): 2-bromo-3-naphthoic acid (*hydrazide*, new m.p. 222°) and its *Me* ester, 3-bromo-2-naphthylurethane, (II), and 2 : 3- $C_{10}H_6Br_2$.

H. G. M.

Amidines derived from quinolines.—See B., 1938, 321.

Spectrochemical investigations in the isoquinoline series. II. E. VARCA and G. VON FODOR (J. pr. Chem., 1938, [ii], 150, 94—98; cf. A., 1937, II, 467).—The absorption spectra of piperon- β -3 : 4-methylenedioxyphenylisopropylamide (max. 2870 and 2580 A.), 6 : 7-methylenedioxy-1-3' : 4'-methylenedi-

oxyphenyl-3-methyl-3 : 4-dihydroisoquinoline (max. 3080, 2720, and 2310 A.), and 2 : 5-diphenyl-4 : 5-dihydro-oxazole (max. 2950, 2790, and 2700 A.) confirm the structure assigned to $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_3\cdot\text{O}_2\text{CH}_2$.

R. S. C.

Synthetical experiments in the paraberine group. II. Synthesis of 17-keto-3 : 12-dimethoxy-6 : 15 : 16 : 17-tetrahydroparaberine. S. N. CHAKRAVARTI and P. L. N. RAO (J.C.S., 1938, 172—175).—*dl*-N-Formyl- β -phenylalanine and CH_2PhCl give *dl*-N-formyl- β -phenyl-N-benzylalanine, m.p. 233°, hydrolysed (HCl) to *dl*- β -phenyl-N-benzylalanine, m.p. 222—225° (decomp.), which could not be converted into tetrahydroparaberine. Mg 3-methoxybenzyl bromide and 3-methoxyphenylacetonitrile afford 3 : 3'-dimethoxydibenzyl, m.p. 61—62°, and a ketone (semicarbazone, m.p. 133°), the oxime of which is reduced electrolytically to α -di-3-methoxyphenylisopropylamine (Ac_2 derivative, m.p. 94°). Et sodiomalonate and 3-methoxybenzyl bromide give a product hydrolysed to *di*-3-methoxybenzylmalonic acid, m.p. 185—186°, which is converted into the acetic acid, m.p. 105° (Ba salt; amide, m.p. 102°). α -Benzamido-3-methoxycinnamic acid, m.p. 178° (decomp.), prepared from 3-methoxybenzaldehyde and hippuric acid, is reduced (Na-Hg) to N-benzoyl- β -3-methoxyphenylalanine, m.p. 144°, hydrolysed to β -3-methoxyphenylalanine (I), m.p. 215° (decomp.). HCO_2H and (I) with 3-methoxybenzyl chloride (II) give N-formyl- β -3-methoxyphenyl-N-3'-methoxybenzylalanine, m.p. 186—188°, hydrolysed to β -3-methoxyphenyl-N-3'-methoxybenzylalanine, m.p. 233°. This compound with CH_2O affords 6-methoxy-N-3'-methoxybenzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline-3-carboxylic acid (III), m.p. 223—225° (Ba salt), also obtained from (II) and 6-methoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline-3-carboxylic acid, m.p. 263—264° (decomp.) [prepared from (I) and CH_2O]. Cyclisation of (III) leads to 17-keto-3 : 12-dimethoxy-6 : 15 : 16 : 17-tetrahydroparaberine, isolated as the semicarbazone, m.p. 250—252° (decomp.).

F. R. S.

Arylamides of hydroxybenzacridonecarboxylic acid.—See B., 1938, 256.

3-Pyrenoline and 2-chrysenoline.—See B., 1938, 258.

Creatininephosphoric acid. Constitution of isocreatininephosphoric acid. K. ZEILE and H. MEYER (Z. physiol. Chem., 1938, 252, 101—114; cf. A., 1935, 1486).—Although short treatment of creatine with POCl_3 gives creatinephosphoric acid, long treatment gives creatininephosphoryl dichloride (I), m.p. 128—131°, identical with the product of interaction of creatinine and POCl_3 . With NH_2Ph (I) gives the corresponding dianilide, m.p. 224—226°, with PhOH the corresponding Ph_2 ester, and (after hydrolysis) with BaCl_2 and CaCl_2 the corresponding Ba and Ca salts. Ca isocreatininephosphate changes spontaneously on keeping for 18 months into Ca creatininephosphate. The dianilide gives 5-p-hydroxy- and -methoxy-benzylidene derivatives, m.p. 205° and 195°, respectively, and with Me_2SO_4 the dianilide, m.p. 176—177°, of 3-methylcreatininephosphoric acid. Similarly, the Ph_2 ester gives the

Ph_2 ester, m.p. 68°, of this acid. With amyl nitrite the methylated Ph_2 ester in AcOH gives the 5-oximino-derivative, m.p. 183°, hydrolysed (HCl) to diphenylphosphoric acid and dimethylparabanic acid. 3-Methylcreatinine hydrochloride with NaNO_2 and HCl gives the hydrochloride, m.p. 128—130°, of the corresponding 3-oximino- and the 5-oximino-derivative, m.p. 230—233°, of dimethylhydantoin which is hydrolysed by HCl to dimethylparabanic acid. Methylation of creatinine by Cornthwaite's method (A., 1937, II, 468) gives methylcreatinine H sulphate (+ H_2O), m.p. 111—112°, with a little of the corresponding Me sulphate, m.p. 145—147°. Reversible ring cleavage occurs when the H sulphate is treated successively with aq. Na_2CO_3 and PhCHO , a substance, m.p. 90°, possibly 5-benzylidene-1 : 3-dimethylhydantoin, being produced together with 5-benzylidenemethylcreatinine.

W. McC.

Effect of specific groups on a reaction mechanism. A. OSKERKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1937, 4, 195—203).—3-Methyl-5-pyrazolone, not tetrolhydrazide, is formed from Et tetrolate and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. Cyclisation is due to the proximity of the triple linking and the CO_2H .

K. S.

4-Amino-1-(4'-sulpho- α -naphthyl)-3-methyl-5-pyrazolone.—See B., 1938, 257.

Chemotherapeutically active piperazine derivatives. D. KOHLBACH (Arh. Hemiju, 1937, 11, 99—123).—N-Phenylpiperazine (I) in aq. HCl and NaNO_2 yield 1-nitroso-4-(p-nitrosophenyl)piperazine, m.p. 155°, reduced by Sn in HCl to N-p-aminophenylpiperazine (II) (trihydrochloride, m.p. >300°; 1 : 4-Bz₂ derivative, m.p. 226.5°). This with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in PhMe gives the Et ester (hydrochloride, m.p. 152—153°) of 4-phenylpiperazineacetic acid (hydrochloride, m.p. 146—147°; amide, m.p. 167—168°). 4-Acetylphenylpiperazine in AcOH at 0° and PhN_2Cl give 4-N-acetyl-piperazinoazobenzene, m.p. 222°, from which 4-N-piperazinoazobenzene, m.p. 162—163°, is obtained by hydrolysis (KOH in EtOH). PhN_2Cl and (I) in HCl yield 4-phenyl-1-benzeneazopyperazine, m.p. 154—154.5°. (II) diazotised and coupled with $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives 4-N-piperazino-2' : 4'-diaminoazobenzene, decomp. 220° [tetrahydrochloride (III)], with 2 : 6-diaminopyridine (IV) gives 4'-N-piperazinobenzeneazo-2 : 6-diaminopyridine [tetra- (V) and tri-hydrochloride], with $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ yields 4'-N-piperazinobenzeneazo-2-naphthol (dihydrochloride), and with 1-phenyl-3-methyl-5-pyrazolone affords 4-(4'-N-piperazinobenzeneazo)-1-phenyl-3-methyl-5-pyrazolone. Diazotised $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ and (IV) give 2 : 6-diamino-3-p-dimethylaminobenzeneazopyridine trihydrochloride (VI). Diazotised $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ (VII) couples with (I), or its 4-Et, -OH, CH_2CH_2 , -Ac, $\text{-CH}_2\cdot\text{CO}_2\text{Et}$, or $\text{-CH}_2\cdot\text{CO}\cdot\text{NH}_2$ derivatives, giving 4-sulphonamido-4'-N-piperazyl- (hydrochloride), 4'-(4''- β -hydroxyethylpiperazino)- [hydrochloride, m.p. 200° (decomp.)], 4'-(4''-acetyl-piperazino)-, 4'-(4''-carbethoxymethylpiperazino)-, and 4'-(4''-carbamylmethylpiperazino)-azobenzene. $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ with (I) affords 4-p-acetamidobenzene-sulpho-1-phenylpiperazine, m.p. 260—262°, hydrolysed to the 4-p- NH_2 -derivative, m.p. 214—215° (hydrochloride, m.p. 169—170°). $\text{NH}(\text{CH}_2\cdot\text{CH}_2\text{Br})_2$ and (VII) give p-N-piperazino-

benzenesulphonamide, m.p. 210—211° (hydrobromide, m.p. 258—259°). The bactericidal action of (III) and (V) is < that of Pyridium, and the streptococcicidal action (*in vivo*) of the above sulphonamides < that of Prontosil. The absorption spectra (λ 4500—6000 Å.) of (V) and (VI), in H₂O and aq. HCl, are determined.

R. T.

1-*n*-Alkyl-5:5-ethylisobutylbarbituric acids. J. S. BUCK, A. M. HJORT, W. S. IDE, and E. J. DEBEER (J. Amer. Chem. Soc., 1938, 60, 461—462).—Compounds of the series 5-ethyl-5-isobutyl-1-*n*-amyl- to -1-*n*-docosyl-barbituric acid are readily prepared, but have no therapeutic val.; the hypnotic effect disappears after the C₈-compound; all are fatal to mice at the min. hypnotic dose. The following are new. *n*-Octyl-, m.p. 102.5°, -nonyl-, m.p. 108°, -decyl-, m.p. 113°, -dodecyl-, m.p. 107°, -tetradecyl-, m.p. 114.5°, and -docosyl-carbamide, m.p. 115°; 5-ethyl-5-isobutyl-1-*n*-amyl-, m.p. 49°, -hexyl-, m.p. 55—56°, -heptyl-, m.p. 52—53°, -octyl-, b.p. 198—200°/2.5 mm., -nonyl-, b.p. 190—193°/0.5 mm., -decyl-, b.p. 215°/1.5 mm., -dodecyl-, m.p. 43°, -tetradecyl-, m.p. 54°, -hexadecyl-, m.p. 60°, -octadecyl-, m.p. 66°, and -docosyl-barbituric acid, m.p. 69°.

R. S. C.

Hexahydrobenzylbarbituric acids. M. M. KATZNELSON and D. A. BRODSKI (Cmpt. rend. Acad. Sci. U.R.S.S., 1937, 17, 477—481).—From Et₂ hexahydrobenzyl-malonate, b.p. 122—124°/4 mm., and -methyl-, b.p. 135—136°/1 mm., -ethyl-, b.p. 171°/20 mm., -propyl-, and -isobutyl-malonate, with NaOEt and CO(NH₂)₂ at about 100°, hexahydrobenzyl-barbituric acid, m.p. 265—266°, and -methyl-, m.p. 223°, -ethyl-, m.p. 161—162°, -propyl-, m.p. 173—174°, and -isobutyl-barbituric acid, m.p. 184°, are obtained.

E. W. W.

Substituted barbituric acids.—See B., 1938, 321.

Structure of dipyrroles. C. F. H. ALLEN, M. R. GILBERT, and D. M. YOUNG (J. Org. Chem., 1937, 2, 227—234).—2-Phenylpyrrole (I) was prepared by isomerisation of *N*-phenylpyrrole (obtained from aniline mucate) in a Pyrex combustion tube heated to dull redness. In other unsuccessful attempts to prepare it, the following have been obtained: β -cyanopropiophenone, m.p. 76° (2:4-dinitrophenyl-hydrazone, m.p. 141°), hydrolysed to CPh·[CH₂]₂·CO₂H (II) (2:4-dinitrophenylhydrazone, m.p. 190°), but not reduced by Stephen's method to the aldehyde. Pyrolysis of the Ca salts of (II) and HCO₂H gave CPhMe. Refluxing (8 hr.) with mineral acid does not affect (I), which gives no picrate or methiodide, but gives 2-phenyl-4:7-dimethylindole with acetylacetone. The production of a pink colour in (I) is due to traces of impurity affected by light. With HCl-Et₂O (I) gives diphenyldipyrrole (III), m.p. 140° [hydrochloride, m.p. 202—203° (decomp.); sulphate, m.p. 210—211° (decomp.); picrate, m.p. 184° (decomp.); methiodide (IV), m.p. 210—211° (decomp.)], unaffected by dil. HCl in H₂O or EtOH; no depolymerisation occurs. With KOH-EtOH (IV) gives an oil which readily reacts with MeI giving a methyl methiodide, m.p. 206—225°, insol. in H₂O. With o-C₆H₄(CO)₂O (III) gives a black oil, and with KMnO₄ gives BzOH, but with O₃ a tar. On the basis of the fore-

going results the structure $\text{CPh}\cdot\text{N}\begin{matrix} \diagup \\ \text{CH}_2\cdot\text{CH}_2 \end{matrix} \text{CH}\cdot\text{C}\begin{matrix} \diagdown \\ \text{CH}\cdot\text{CH} \end{matrix} \text{NH}\cdot\text{CPh}$ is proposed for (III), and is regarded as typical for dipyrroles.

H. G. M.

Syntheses in the pyrazine series. I. Curtius and Hofmann degradation of pyrazine-2:5-dicarboxylic acid. P. E. SPOERRI and A. ERIKSON (J. Amer. Chem. Soc., 1938, 60, 400—402).—Attempts to prepare diaminopyrazines failed. Pyrazine-2:5-dicarboxyl dichloride, m.p. 143—144°, does not react with NaN₃ in C₆H₆. Me₂ pyrazine-2:5-dicarboxylate (prep. by MeOH-HCl), m.p. 168—169°, and N₂H₄·H₂O in MeOH give the dihydrazide, m.p. 270°, converted by HNO₂ into the diazide, decomp. 133—134°, and thence by EtOH into the diurethane, m.p. >270°, which resists fuming HCl at 210°, conc. H₂SO₄, and KOH. In boiling C₆H₆ the diazide yields the diisocarbimide, m.p. 250°, which could not be hydrolysed. The diamide, m.p. >270°, prepared from the ester, is stable to HOCl and HOBr.

R. S. C.

Pyrazine derivatives.—See B., 1938, 257.

Quinazolines.—See B., 1938, 257.

Compounds of dipyrpydyl salts with metallic salts. B. EMMERT and H. LAURITZEN (Ber., 1938, 71, [B], 240—242).—Agitation of a solution of excess of the requisite dipyrpydyl alkiodide with freshly pptd. AgI yields the salts, C₁₀H₈N₂·2MeI, 2AgI; C₁₀H₈N₂·2CH₂PhI, 2AgI; C₁₀H₈N₂·2PhI, 3AgI; C₁₀H₈N₂·MeI, AgI; C₁₀H₈N₂·2CH₂PhBr, 3AgBr. Their formation from very dil. solution and their stability are remarkable. Compounds (1:1) of AgI with 2-methylpyridine methiodide, quinoline methiodide, and acridine methiodide and of quinoline benzylbromide with AgBr (1:1) are described. The following very stable and highly insol. substances have been prepared: C₁₀H₈N₂·2MeI, 2CuI; C₁₀H₈N₂·2CH₂PhI, 4CuI; C₁₀H₈N₂·2PhI, 6CuI; C₁₀H₈N₂·MeI, 2CuI; C₁₀H₈N₂·2CH₂PhBr, 2CuBr; C₁₀H₈N₂·2CH₂PhCl, 2CuCl; C₁₀H₈N₂·2MeI, 3HgI₂; C₁₀H₈N₂·2MeI, 4PbI₂; C₁₀H₈N₂·2PhI, 2PbI₂; C₁₀H₈N₂·MeI, 2PbI₂; C₁₀H₈N₂·2MeI, 2CdI₂.

H. W.

Compounds of skatole with benzaldehyde. V. DOSTÁL (Chem. Listy, 1938, 32, 13—15).—Skatole and PhCHO in EtOH with H₂SO₄ (24 hr. at room temp.) yield phenylbis-(3-methyl-2-indolyl)methane, oxidised by HNO₂ to yellow phenylbis-(3-methyl-2-indolyl)carbinol, m.p. 80°, converted into a red isomeride, +H₂O, by pptn. with NaOH, and into the hydrochloride of phenyl-3-methyl-2-indolyl-3'-methyl-2'-indolidenemethene, m.p. 140° (decomp.), by pptn. with HCl, from EtOH solution.

R. T.

ang- and lin-Anthraquinonetriazole. H. WALDMANN and K. G. HINDENBURG (Ber., 1938, 71, [B], 371—372).—Diazotisation of 1:2-diaminoanthraquinone in conc. H₂SO₄ at 10° gives ang-anthraquinonetriazole, $\frac{1}{2}$ or $\frac{2}{1}$ > C₁₂H₆O₂ < $\begin{matrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{matrix}$ > N, m.p. >330° (N-Ac derivative, m.p. 266°). lin-Anthraquinonetriazole (N-Ac derivative, m.p. 210°) is derived similarly from 2:3-diaminoanthraquinone. H. W.

C-Nitrotetrazole.—See B., 1938, 323.

Action of phenylhydrazine on carbon-carbon linkings. M. PASSERINI and V. CASINI (Gazzetta, 1937, 67, 785—790).—NHPH·NH₂ converts 4:4'-benzylidenebis-(1-phenyl-3-methyl-5-pyrazolone) or 4-benzylidene-1-phenyl-3-methyl-5-pyrazolone into 1:1'-diphenyl-3:3'-dimethyl-5:5'-diketotetrahydro-4:4'-dipyrzazolyl (I), no m.p. <320°, and NHPH·N·CHPh (II). The corresponding methenyl-bispyrazolone also yields (I), with 1-phenyl-3-methyl-5-pyrazolone-4-aldehyde anil, m.p. 153—155°. Benzylidenebisantipyrine does not react. Benzylidene- and methenyl-bis-(2-methylindole) give only 2-methylindole, the former with (II). Styrene gives (II).

E. W. W.

1-Substituted pyridino-(2':3'-4:5)-2:1:3-triazoles. G. CHARRIER and M. IORIO (Atti R. Accad. Lincei, 1937, [vi], 26, 170—175).—2:6-Diamino-3-benzeneazo- and -3-(2'-butoxy-5'-pyridineazo)-pyridine dehydrogenated by the method of Schmidt and Hagenböcker (A., 1921, i, 897) give respectively 6'-amino-1-phenyl-, m.p. 215°, and -1-(2'-butoxy-5'-pyridyl)-pyridino-(2':3'-4:5)-2:1:3-triazole, m.p. 212°. These compounds can be diazotised and coupled. The former with 1:2:4-C₆H₃Cl(NO₂)₂ gives 6'-(2':4'-dinitroanilino)-1-phenylpyridino-(2':3'-4:5)-2:1:3-triazole; the latter reacts similarly. The products thus obtained are reduced by Na₂S.

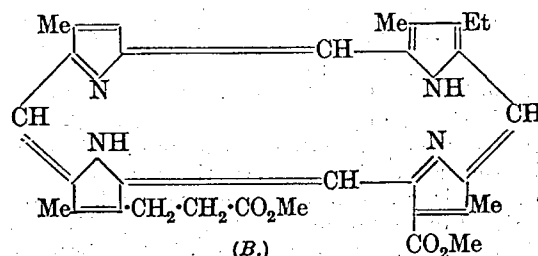
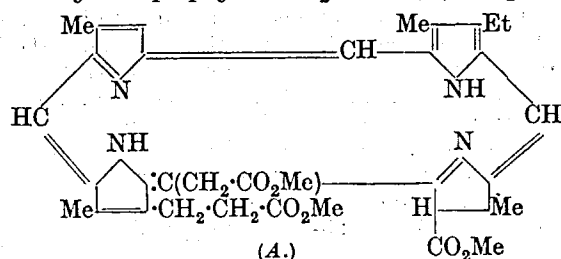
E. W. W.

Azine compounds derived from [3:3']-diaminobenzidine. L. D. TIWARI and S. DUTT (Proc. Nat. Acad. Sci. India, 1937, 7, 58—64).—3:3'-Diaminobenzidine condenses with *o*-diketones in boiling AcOH to dyes which give intense coloration in conc. H₂SO₄. The dyes are reprecipitated by adding H₂O and then dye wool yellow. This behaviour is explained by Dutt's mol. strain theory of colour (cf. A., 1926, 830). The following compounds mostly do not melt but sublime with partial decomposition: (3:4:3':4'-diphenyl)-di-β-naphtho-, -diacenaphtho-, -diphenanthra-, -di-isatin-, -dicarboxydibenzyl- (m.p. 235—236°), -di-*m*-nitroisatin-, -diparaban-, -dialloxan-, and -tetramethyl-quinoxaline-, -di-*o*-nitrophenyl-, m.p. 221—222°, -di-*p*-tolyl-, -di-*o*-chlorophenyldihydroimidazole-, -dihydrophenazine.

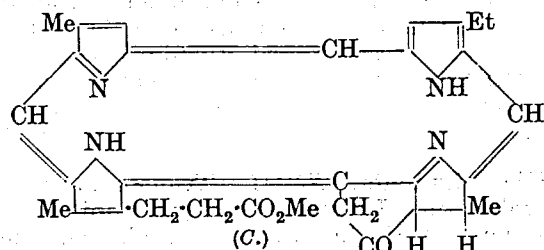
R. G.

Chlorophyll. LXXXI. Devinyl compounds in the chlorophyll-*a* and -*b* series. H. FISCHER and A. WUNDERER (Annalen, 1938, 533, 230—254).—The prep. of the Fe complex salts of phaeophorbide-*a* (I), methylphaeophorbide-*a* (II), C₃₆H₃₆O₅N₄ClFe, m.p. >320°, pyrophaeophorbide-*a* (III), methylpyrophaeophorbide-*a* (IV), C₃₄H₃₄O₃N₄ClFe, m.p. >320°, phaeophorbide-*b*, methylphaeophorbide-*b*, m.p. >320°, pyrophaeophorbide-*b*, m.p. >320°, methylpyrophaeophorbide-*b* (V), m.p. >320°, chlorin *e*₆ Me₃ ester (VI), C₃₇H₄₀O₆N₄ClFe, m.p. 169°, and chlorin *e*₄ Me₂ ester (VII), C₃₅H₃₈O₄N₄ClFe, m.p. 182°, is described. Methylpyrophaeophorbide-*a* Cu salt, C₃₄H₃₄O₃N₄Cu, m.p. >320°, and phaeophorbide-*a* Cu salt, m.p. >320°, have been obtained. Fusion of (I), completely free from acid, with resorcinol at 180—190° gives mainly 2-de-ethylpyrroporphyrin and 2-de-ethylphyloerythrin with spectroscopic amounts of 2-devinylphaeophorbide. With (II) the yield of porphyrin is relatively small, the chief products being

substances of the phaeophorbide type. Analogously (III) is converted almost completely into porphyrins which are scarcely formed from (IV). Esterification with MeOH therefore enhances the stability of the haemins. Generally during fusion with resorcinol the CO₂Me residue at C₁₀ is readily replaced by H and hence (IV) is the best source for the prep. of 2-devinylpyrophaeophorbide-*a*, m.p. 173°. (II) can also be employed if the experiment is prolonged at 190—200°. 2-Devinylpyrophaeophorbide-*a* Me ester with HI-AcOH at 70° gives 2-de-ethylphyloerythrin Me ester, m.p. 252° (corresponding haemin). 2-Devinylpyrophaeophorbide-*a* Me ester haemin, m.p. 184°, 2-devinylpyrophaeophorbide-*a* Me ester oxime, m.p. 244°, and 2-bromodevinylpyrophaeophorbide-*a* Me ester, decomp. 256° after softening at 200°, are described. (VI) is transformed by resorcinol at 168—170° into 2-devinylchlorin *e*₆ Me₃ ester (A), m.p. 199°, and 2-de-ethylrhodoporphyrin Me₂ ester (B), m.p. 238°.



Similarly (VII) is converted into 2-devinylchlorin *e*₄ Me₂ ester which could not be caused to crystallise and 2-de-ethylchloroporphyrin-*e*₄ Me₂ ester, C₃₃H₃₆O₄N₄, m.p. 249°. Attempts to acetylate the devinyl compounds were unsuccessful. Fusion of (V) with resorcinol gives 3-deformyl-2-devinylpyrophaeophorbide-*b* Me ester (C), m.p. 221° (oxime; compound C₃₁H₃₀O₃N₄Br₂), converted by HI in AcOH at 60°



into 3-demethyl-2-de-ethylphyloerythrin Me ester, C₃₁H₃₀O₃N₄, m.p. 232° (Br-derivative). Treatment of 2-deformyl-2-devinylpyrophaeophorbide-*b* Me ester haemin with Ac₂O and SnBr₄ gives a non-cryst. substance the spectrum of which, with those of the corresponding oxime and Br-derivative, is described.

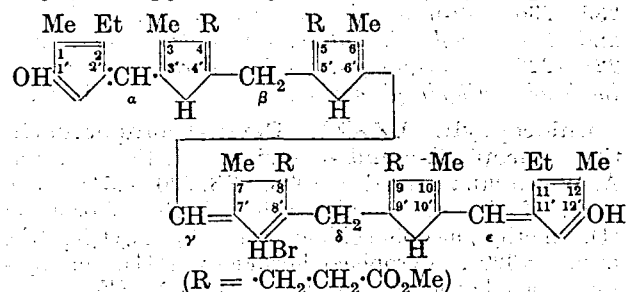
H. W.

Bile pigments. XVII. Pyrrolines, opsopyrrolealdehyde, and a new synthesis of isoneoxanthobilirubic acid. H. FISCHER and H. HÖFELMANN (Z. physiol. Chem., 1938, 251, 187—197).—Treatment of cryptopyrrole (I) with Zn dust and HCl gives *cryptopyrroline* (II), separated from unchanged (I) by use of KH_2PO_4 . (II), b.p. $59^\circ/11$ mm., is stable to air when free from (I), gives a positive reaction with KMnO_4 , and decolorises Br. The *picrate*, m.p. 166° , *picrolonate*, m.p. 203° , and *styphnate*, m.p. 131° , are described. CrO_3 and HNO_3 are without action on (II) whereas non-characteristic decomp. is caused by fuming HNO_3 ; in no case could methylethylmaleimide (III) be isolated, in harmony with the negative results of the oxidation of stercobilin. Attempts to condense (II) with cryptopyrrolealdehyde (IV) in presence of a little HBr gave essentially the auto-condensation product of (IV). The attempted condensation with HCO_2H —HBr did not yield a pyrrromethene. Attempts to introduce $\cdot\text{CHO}$ were unsuccessful. Catalytic reduction (PtO_2 in AcOH) of (II) yields *cryptopyrrolidine* (*picrate*, m.p. 135° ; *picrolonate*, m.p. 213° ; *styphnate*, m.p. 152°). Opsopyrrole (V) is reduced similarly to *opsopyrroline*, b.p. $54^\circ/11$ mm. (*picrate*, m.p. 158°), which does not yield (III) when oxidised; it gives a very hygroscopic product, m.p. 156° , with $\text{CHN}_2\cdot\text{CO}_2\text{Et}$ and a *di-bromide*, m.p. 163° . 2:3-Dimethylpyrrole analogously affords 2:3-*dimethylpyrroline*, b.p. $42^\circ/11$ mm. (*picrate*, m.p. 160°). Under strictly defined conditions (V) is converted into 3-methyl-4-ethylpyrrole-2-aldehyde (VI), m.p. 80° , the constitution of which follows from its bromination to 5-bromo-3-methyl-4-ethylpyrrole-2-aldehyde (VII), m.p. 136° , differing from 2-bromo-3-methyl-4-ethylpyrrole-5-aldehyde, m.p. 115° , of Siedel and Fischer (A., 1933, 404); the *aldazine* has m.p. 195° . It is reduced to homogeneous hæmopyrrole (VIII). Condensation of (VII) with (VIII) leads to 5-bromo-3:4':5'-trimethyl-4:3'-diethylpyrromethene hydrobromide, m.p. 229° (corresponding free base, m.p. 124 — 125°). Me opsopyrrolecarboxylate and (VII) yield 5-bromo-3:3'-dimethyl-4-ethyl-4'- β -carbomethoxyethylpyrromethene hydrobromide (IX), m.p. 198° , whereas opsopyrrolecarboxylic acid gives the corresponding acid, (X), decomp. about 230° . With NaOMe (IX) or (X) gives isoneoxanthobilirubic acid, m.p. 238 — 239° . Reduction (Wolff-Kishner) of the crude product, m.p. 55° , obtained under somewhat different conditions in attempts to obtain (VI) leads to a mixture of hæmo- and crypto-pyrrole, showing that CHO can enter at $\text{C}_{(2)}$ as well as at $\text{C}_{(5)}$, and thus explaining the differing results of Siedel (A., 1935, 631). H. W.

Bile pigments. XVIII. Transformation of coprohæmin I into coproglaucobilin. H. FISCHER and H. LIBOWITZKY (Z. physiol. Chem., 1938, 251, 198—203).—Coprohæmin ester I in $\text{C}_5\text{H}_5\text{N}$ is smoothly reduced by ascorbic acid to its hæmochromogen. Passage of O_2 through the system leads through an unexplored intermediate to a dark green solution with a three-banded absorption spectrum of the type of verdohæmochromogen. The product can be transferred to CHCl_3 but has not been obtained cryst. Treatment of the CHCl_3 solution

with 10% HCl leads to the non-cryst. verdohæm. Cautious removal of Fe from the coloured complex gives the very unstable, non-cryst. parent pyrrole pigment which readily undergoes change giving, *inter alia*, *coproglaucobilin ester* Ia [Me_4 1':8'-*dihydroxy*-1:3:5:7-tetramethylbilin-2:4:6:8-tetrapropionate] (I), m.p. 214° . The isomeric *coproglaucobilin ester*, III γ [Me_4 1':8'-*dihydroxy*-1:3:6:8-tetramethylbilin-2:4:5:7-tetrapropionate] (II); m.p. 186° , is obtained by dehydrogenation of coprobilirubin IV γ with Br and subsequent esterification. The absorption spectra of (I) and (II) are very closely similar, the differences being of the same type and magnitude as those observed between isomeric pyrrromethenes. Both esters in MeOH give with $\text{Zn}(\text{OAc})_2$ green Zn salts, converted by I-EtOH into blue compounds with intense red fluorescence. Hydrolysis of the esters and reduction with Na-Hg leads to the colourless coprobilirubins with intense positive Ehrlich reaction. The spectra of the isomerides are identical. Reduction of (I) with Zn dust—AcOH gives yellow, cryst. coprobilirubin Ia in small amount; oxidation of its ammoniacal solution by air causes an intense pent-duopent reaction. The bile compound nature of the blue substance is thus firmly established and a cryst. bile pigment is obtained for the first time *in vitro* from a hæmin and by a method which is possible in the living cell. Cryst. products have not yet been obtained from tetramethylhæmatoporphyrin-Fe salt or hæmin IX Me_2 ester. Mesohæmin ester IX gives a mixture of glaucobilin esters of ill-defined m.p. but the immediate precursor of these is cryst. II. W.

Bile pigments. XIX. Hexapyrrenes. H. FISCHER and H. REINECKE (Z. physiol. Chem., 1938, 251, 204—217).—Condensation of neoxanthobilirubic acid (I) with 3:3-dimethyl-5:5'-dibromomethyl-4:4'-di- β -carboxyethylpyrromethene hydrobromide (II) gives 1':12'-*dihydroxy*-1:3:6:7:10:12-hexamethyl-2:11-diethyl-4:5:8:9-tetra- β '-carbomethoxyethyl- β 8-hexapyrrene hydrobromide (III), m.p. 250° .



The corresponding free base (IV), m.p. 242° after becoming discoloured at 210° , couples with PhN_2Cl to the azo-dye of (I) and gives neoxanthobilirubic ester when fused with $m\text{-C}_6\text{H}_4(\text{OH})_2$. Dehydrogenation of (III) in acid medium gives a no. of pigments among which glaucobilin Me_2 ester is identified. Dehydrogenation of (IV) with $\text{Cu}(\text{OAc})_2$ in CHCl_3 —MeOH gives the compound, $\text{C}_{55}\text{H}_{62}\text{O}_{11}\text{N}_6\text{Cu}_2$, m.p. 296° , which with conc. HCl in CHCl_3 gives the substance, $\text{C}_{55}\text{H}_{66}\text{O}_{11}\text{N}_6$, m.p. 236° . By $\text{NH}_2\text{OH}\cdot\text{HCl}$ in AcOH (IV) is dehydrogenated and then converted by CH_2N_2 into the compound, $\text{C}_{55}\text{H}_{66}\text{O}_{12}\text{N}_6$. Catalytic hydrogenation of (I) in MeOH leads to the production

of porphyrins. Condensation of (I) with 3:3'-dimethyl-5:5'-dibromomethyl-4-ethyl-4'- β -carboxyethylpyrromethene hydrobromide gives 1':12'-dihydroxy-1:3:6:7:10:12-hexamethyl-2:5:11-triethyl-4:8:9-tri- β -carbomethoxyethyl- $\beta\delta$ -tetrahydrohexapyrrene hydrobromide, m.p. 249° [free base, m.p. (indef.) 225–230°]. *Ætioneoxanthomesobilirubin* and (II) yield 1':12'-dihydroxy-1:3:6:7:10:12-hexamethyl-2:4:9:11-tetraethyl-5:8-di- β -carbomethoxyethyl- $\beta\delta$ -tetrahydrohexapyrrene hydrobromide, m.p. 260° (free base). *Coproneoxanthobilirubin* acid [5-hydroxy-3:3'-dimethylpyrromethene-4:4'-dipropionic acid], m.p. 282° (decomp.) (Me_2 ester, m.p. 198°; azo-dye from PhN_2Cl , m.p. 185°), is obtained by brominating opsopyrrolecarboxyaldehyde, condensation of the bromo-opsopyrrolecarboxyaldehyde, m.p. 178°, with opsopyrrolecarboxylic acid, and treatment of the methene so formed with NaOMe in MeOH; it is condensed with (II) to 1':12'-dihydroxy-2:3:6:7:10:11-hexamethyl-1:4:5:8:9:12-hexa- β -carbomethoxyethyl- $\beta\delta$ -tetrahydrohexapyrrene hydrobromide. Me_2 5-hydroxy-4:4'-dimethylpyrromethene-3:3'-dipropionate is transformed by HCl and HCN in $CHCl_3$ into Me_2 5-hydroxy-5'-formyl-4:4'-dimethylpyrromethene-3:3'-dipropionate, m.p. 201°, which does not condense as expected with 3:3'-dimethyl-4:4'-di- β -carboxyethylpyrromethene hydrobromide; the product has an intense glaucobilin spectrum.

II. W.

ms-Methylpyrromethenes. H. FISCHER and H. HÖFELMANN (Z. physiol. Chem., 1938, 251, 218–225).—5-Acetyl-2-methylpyrrole (I) with 2:4-dimethylpyrrole (II) in presence of 48% HBr at 100° yields ms-5:3':5'-tetramethylpyrromethene hydrobromide, $\begin{array}{c} CH-CH \\ CMe-NH \end{array} > C-CMe < \begin{array}{c} CMe-CH \\ N=CMe \end{array}$, m.p. 212°. It does not crystallise readily and retains ash very obstinately. The free base could not be isolated and a picrate does not appear to exist. Analogous condensation of (I) with 2:3:4-trimethylpyrrole, cryptopyrrole (III), *Me* hæmopyrrolecarboxylate or the corresponding acid (IV), or with 4-methyl-2-ethylpyrrole (V) affords respectively the hydrobromides of ms-5:3':4':5'-pentamethylpyrromethene, m.p. 225°, ms-5:3':5'-tetramethyl-4'-ethylpyrromethene, m.p. 205°, ms-5:4':5'-tetramethyl-3'- β -carbomethoxyethylpyrromethene, m.p. 146°, ms-5:4':5'-tetramethyl-3'- β -carboxyethylpyrromethene, m.p. 180° after softening, and ms-5:3'-trimethyl-5'-ethylpyrromethene, m.p. 170°. Similarly, 5-acetyl-2:3-dimethylpyrrole with (II), (V), (IV), and (III) respectively yields the hydrobromides of ms-4:5:3':5'-pentamethylpyrromethene, m.p. (indef.), 220–222° after darkening at 150°, ms-4:5:3'-tetramethyl-5'-ethylpyrromethene, m.p. 173°, ms-4:5:4':5'-pentamethyl-3'- β -carboxyethylpyrromethene, m.p. 202–203°, and ms-4:5:3':5'-pentamethyl-4'-ethylpyrromethene, m.p. 193°. Successive addition of ethylpyrrole (VI) and AcBr in Et_2O to $MgEtBr$ affords 5-acetyl-2-ethylpyrrole, m.p. 44°, which condenses with (II) to ms-3':5'-trimethyl-5-ethylpyrromethene hydrobromide, m.p. 192°. The attempted ring synthesis of (VI) from *Et* propionylacetate, $(C_2H_5Cl)_2O$, and NH_3 led, after hydrolysis, to 2-ethylfuran-3-carboxylic acid, m.p. 43°;

after distillation under diminished pressure (b.p. 123°/11 mm.) it has m.p. 66° after softening at 38° and is probably dimeric. Treatment of *Et* 2:3-dimethylpyrrole-4-carboxylate and $CH_2(CN)_2$ in $Et_2O-CHCl_3$ with HCl leads, after hydrolysis, to *Et* 5- ω -cyanoacetyl-2:3-dimethylpyrrole-4-carboxylate, m.p. 189°, which could not be condensed satisfactorily.

H. W.

Benzoporphin. III. Action of metals on ω -cyanoacetophenone and on 3-methylphthalimidine. Synthesis of tetrabenzoporphin. J. H. HELBERGER, A. VON REBAY, and D. B. HEVER (Annalen, 1938, 533, 197–215; cf. A., 1937, II, 471).— ω -Cyanoacetophenone (I) and Mg at high temp. in presence of quinoline give much decomposed product and very small amounts of Mg complex salts from which by chromatographic analysis a product, $C_{34}H_{18}N_6MgH_2O$, m.p. >370°, is isolated. This is comparatively freely sol. in C_5H_5N to a green solution with intense red fluorescence. It gives a well-defined band spectrum. The poorness of the yield appears essentially due to H_2O eliminated during the change. Protracted treatment of (I) with boiling H_2O gives acetophenone- ω -carboxylamide, m.p. 152°, apparently isomeric with the compound, m.p. 116.5°, of Karslake and Huston (A., 1909, i, 301). This gives dyes of the tetrabenzozaporphin series only in spectroscopic amount. Above 100° it loses H_2O giving not (I) but a very hygroscopic substance of high mol. wt., probably a polymeride of methylenephthalimidine. Treatment of (I) with Fe powder in a little quinoline for several hr. at >200° gives NH_3 , H_2O , and phthalimide with the compounds, $C_{34}H_{18}N_6Fe2C_5H_5N$, $C_{35}H_{19}N_5Fe2C_5H_5N$, and $C_{36}H_{20}N_4Fe2C_5H_5N$ which resemble one another very closely. Their adsorption by Al_2O_3 is more pronounced as the % N increases. Their spectroscopic behaviour is very similar to that of the imidoporphyrins. Methylphthalazone in $EtOH$ is hydrogenated (Raney Ni) at 200–220°/100 atm. to methylphthalimidine (II), m.p. 115°. Catalytic hydrogenation of the inner anhydride of acetophenone-oxime- ω -carboxylic acid proceeds at a lower temp. but the yields are lower owing to simultaneous elimination of NH_3 . Treatment of (II) with Mg at about 200° gives essentially decomp. products whereas if the mixture is heated rapidly to about 300° the Mg complex salt of tetrabenzoporphyrin is obtained. This when treated with conc. H_2SO_4 followed by H_2O gives the free tetrabenzoporphyrin (III), $C_{36}H_{22}N_4$; the green solution, which has a small red fluorescence in quinoline, gives a well-defined band spectrum. Reaction occurs also between (II) and other metals (e.g., Zn, Fe, Cu) but better results are obtained by use of oxides or acetates. Thus (II) and $Zn(OAc)_2$ evolve AcOH at 200°, giving a blood-red mass which becomes dark green at about 300° giving the complex (IV), $C_{36}H_{20}N_4Zn$, in 12% yield. The compound, $C_{36}H_{20}N_4Fe$, and the *Mn* compound are obtained similarly but $Cu(OAc)_2$ does not react thus. The complex salts of (III) show many analogies to the corresponding derivatives of phthalocyanine. Thus they retain H_2O of crystallisation very tenaciously and sublime readily and apparently without decomp. at a high temp. They are, however, more stable towards oxidising agents. Thus (IV) is partly un-

decomposed by conc. HNO_3 ; after 12 hr. at 100° , the acid solution contains $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NH}$ and $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$. H. W.

Co-ordination of metalloporphyrins with nitrogenous bases.—See A., 1938, I, 196.

Violacein, the pigment of *Bacillus violaceus*. II. F. WREDE and W. SWANE (Arch. exp. Path. Pharm., 1937, 186, 532—538).—Violacein, $\text{C}_{42}\text{H}_{28}\text{O}_7\text{N}_6$ (A., 1934, 536), gives additive compounds with 2 mols. of $\text{C}_6\text{H}_5\text{N}$ and of 2-chloropyridine, and with 1 mol. of NH_2Ph and of $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$; none of these has m.p. $<300^\circ$. The Ac derivative (*loc. cit.*) has 6 OAc. T. B. H.

Absorption spectra of typical unsymmetrical cyanine dyes.—See A., 1938, I, 116.

Oxazolines and thiazolines. III. Action of ethylene chlorohydrin on thiocyanates. P. G. SERGEEV, B. S. KOLITSHEV, and A. G. KONDRATIEV (J. Gen. Chem. Russ., 1937, 7, 2600—2604).— $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ and KCNS at 100° yield 2-thion-3- β -hydroxyethyltetrahydroglyoxaline (Ag salt) and 2-thioltetrahydro-oxazole. R. T.

3-Acylisooxazole compounds. I. T. AJELLO (Gazzetta, 1937, 67, 779—785).—3-Benzoyl-5-phenylisooxazole with $\text{NH}_4\text{OH}\cdot\text{HCl}$ gives, in addition to its oxime (A., 1938, II, 71), 3-phenyl-4-phenacyl-1 : 2 : 5-oxadiazole, m.p. 137° [oxime, m.p. 142° (Bz derivative, m.p. 125°)], hydrolysed by conc. $\text{KOH}\cdot\text{EtOH}$ to 3-phenyl-4-methyloxadiazole and EtOBz . E. W. W.

Doebner reaction. XIII. R. CRUSA and V. D'AMATO (Gazzetta, 1937, 67, 776—778; cf. A., 1936, 1393).—Furfuraldehyde, AcCO_2H , and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OR}$ (R = H, Me, or Et) in EtOH give 6-hydroxy-, m.p. $302\text{--}305^\circ$ (decomp.), 6-methoxy- (+ H_2O), m.p. 240° (decomp.), and 6-ethoxy-, m.p. $215\text{--}216^\circ$ (decomp.), and, using $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, 8-ethoxy-2-(2'-furyl)cinchonic acid, m.p. $150\text{--}151^\circ$ (decomp.) [Na salt (+ $2\text{H}_2\text{O}$); Et ester, m.p. 67°]. E. W. W.

Isosteric and structurally analogous compounds. VI. Derivatives of thiazole and oxazole. H. ERLMEYER and A. KLEIBER (Helv. Chim. Acta, 1938, 21, 111—113).—Treatment of $\text{CMe}_2\text{Br}\cdot\text{CO}_2\text{H}$ with NH_4 dithiocarbamate (I) in EtOH at 60° gives 4-keto-2-thion-5 : 5-dimethylthiazolidine, m.p. 129° , whereas $\text{CEt}_2\text{Br}\cdot\text{CO}_2\text{H}$ similarly yields 4-keto-2-thion-5 : 5-diethylthiazolidine, m.p. 106° . 5-Ethylrhodanine and $\text{CH}_3\text{CH}\cdot\text{CH}_2\text{Br}$ in alkaline solution afford 4-keto-2-thion-5-ethyl-3-allylthiazolidine, b.p. $160^\circ/11\text{ mm.}$, which does not give CNS' when degraded with alkali. 5-Phenylrhodanine, from (I) and $\text{CHPhBr}\cdot\text{CO}_2\text{H}$, gives 4-keto-2-thion-5-phenyl-3-allylthiazolidine, m.p. 118° , which on further treatment with $\text{CH}_3\text{CH}\cdot\text{CH}_2\text{Br}$ and alkali gives 4-keto-2-thion-5-phenyl-3 : 5-diallylthiazolidine, b.p. $205\text{--}207^\circ/10\text{ mm.}$ $\text{CH}(\text{OEt})_2\cdot\text{CO}_2\text{Et}$ and guanidine in EtOH yield 2-imino-4-keto-5 : 5-diethylloxazolidine, m.p. 237° , converted by warm 30% H_2SO_4 into 2 : 4-diketo-5 : 5-diethylloxazolidine, b.p. $157^\circ/12\text{ mm.}$ H. W.

Synthesis of antimalarials. (Dialkylamino-alkyl)amino-derivatives of the benzthiazole series. I. L. KNUNIANZ and Z. V. BENEVOLENSKAJA

(J. Gen. Chem. Russ., 1937, 7, 2471—2477).—3-Nitro-4-acetamidoanisole and P_2S_5 in boiling C_6H_6 solution afford 3-nitro-4-thiolacetamidoanisole, m.p. $101\text{--}102^\circ$, which with $\text{K}_3\text{Fe}(\text{CN})_6$ in 10% KOH gives 3-nitro-5-methoxy-1-methylbenzthiazole, m.p. $149\text{--}150^\circ$, reduced by SnCl_2 in HCl to the 3- NH_2 -compound, m.p. $95\text{--}96^\circ$ (hydrochloride, m.p. $214\text{--}216^\circ$): this with $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ (I) (8 hr. at $130\text{--}140^\circ$) gives 3-(γ -diethylaminopropyl)amino-5-methoxy-1-methylbenzthiazole (II), b.p. $209\text{--}210^\circ/2\text{ mm.}$ (hydrochloride, m.p. $185\text{--}187^\circ$). 3-Nitro-4-formamidoanisole, m.p. $150\text{--}151^\circ$, is converted as above into 3-nitro-4-thiolformamidoanisole, m.p. $180\text{--}182^\circ$, not yielding a benzthiazole derivative with $\text{K}_3\text{Fe}(\text{CN})_6$ in aq. NaOH . 3-Nitro-4-aminoanisole and $\text{Et}_2\text{C}_2\text{O}_4$ (4 hr. at 180°) yield the Et ester, m.p. 157° , of 3-nitro-4-oxamidoanisole, which with K_2S and P_2S_5 gives 3-nitro-4-thioloxamidoanisole, m.p. 132° (Et ester, m.p. 80°). This is converted as above into 3-nitro-5-methoxybenzthiazole-1-carboxylic acid, which when boiled with 5% HCl gives 3-nitro-5-methoxybenzthiazole, m.p. 151° , reduced by SnCl_2 in HCl to the 3- NH_2 -derivative, m.p. 151° (hydrochloride, m.p. $206\text{--}208^\circ$). This condenses with (I) to give 3-(γ -diethylaminopropyl)amino-5-methoxybenzthiazole, b.p. $215\text{--}218^\circ/4\text{ mm.}$; this and (II) have no plasmocidal action. R. T.

Synthetic vitamin- B_1 . T. IMAI and K. MAKINO (Z. physiol. Chem., 1938, 252, 76—80).—6-Amino-2-methyl-5-aminomethylpyrimidine hydrochloride with KNO_2 or NaNO_2 at $65\text{--}67^\circ$ gives the corresponding alcohol, m.p. 195° which, in AcOH with HBr gives 6-amino-2-methyl-5-bromomethylpyrimidine hydrobromide, m.p. $208\text{--}209^\circ$; this with 4-methyl-5-hydroxyethylthiazole at 125° gives aneurin hydrobromide, converted, by way of the picrolonate, m.p. $226\text{--}228^\circ$, into the hydrochloride. Alternatively, 6-amino-2-methyl-5-aminomethylpyrimidine is treated with HCS_2K and the product, m.p. 190° , with Me α -chloro- γ -hydroxypropyl ketone gives low yields of aneurin. Aneurin is also obtained from 6-amino-5-thioformamidomethylpyrimidine and Me α -chloro- γ -acetoxypropyl ketone. W. McC.

Alkaloids of *Heliotropium lasiocarpum*. Structure of heliotridane, and synthesis of dl-heliotridane. G. P. MENSCHIKOV (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 1035—1048).—The base $\text{C}_9\text{H}_{15}\text{N}$ (A., 1935, 1255) is reduced ($\text{Zn}\text{--}\text{HCl}$) to a pyrroline base, $\text{C}_9\text{H}_{17}\text{N}$, b.p. $165\text{--}166^\circ$, hydrogenated (Adams) to dl-dihydrode-N-methylheliotridane (I), b.p. $163\text{--}164^\circ$ (picrate, m.p. $114\text{--}115^\circ$; picrolonate, m.p. $158\text{--}160^\circ$). This is boiled for 40 min. with MeI in MeOH, the solvent is distilled off, the residue is dissolved in H_2O , extracted with Et_2O , and AgOH is added to the aq. layer. The solution is filtered after 12 hr., the H_2O is distilled off, the residue is dissolved in Et_2O , and the solution is extracted with 2% HCl . The aq. extract when hydrogenated (Pt catalyst) yields dl-tetrahydrode-N-methylheliotridane, b.p. $180\text{--}181^\circ$ (platinichloride, m.p. $133\text{--}134^\circ$; picrolonate, m.p. $93\text{--}94\cdot5^\circ$), identical with the product obtained by the Hofmann degradation of 1-methyl-2-sec-butylpyrrolidine (II) (A., 1938, II, 28), and being δ -dimethylamino- γ -methylheptane. Since (II), 1-methyl-n- and -iso-butylpyrrolidine have been shown

to be different from (I) (A., 1936, 1130; 1938, II, 28), it follows that (I) must be 1:3-dimethyl-2-*n*-propylpyrrolidine, which could arise only from the Hofmann degradation of 1-methylpyrrolisidine; this is therefore identical with heliotridane. 2-*sec*.-Butylpyrrolidine is added to aq. NaOBr at -5° , and the bromoamine formed is heated with conc. H_2SO_4 (5 hr. at $20-150^{\circ}$); this gives *dl*-heliotridane (picrate, indistinguishable from that of the natural substance).

R. T.

Senecio alkaloids. V. Constitution of seneciphylline. R. KONOVALOVA and A. ORÉKHOV (Bull. Soc. chim., 1937, [v], 4, 2037—2042).—Seneciphylline, new formula $\text{C}_{13}\text{H}_{23}\text{O}_5\text{N}$, new $[\alpha]_D -134.2^{\circ}$ in CHCl_3 , is now extracted from *S. stenocephalus*, in which it is the only alkaloid (cf. A., 1935, 764). It is converted by *n*-NaOH into retronecine (I) (A., 1932, 286; 1935, 365), $[\alpha]_D +53^{\circ}$ in EtOH, and *seneciphyllic acid*, $\text{C}_{10}\text{H}_{14}\text{O}_5$, m.p. $140-141^{\circ}$, α 0° , dibasic. Trichodesmidine (A., 1936, 88) is identical with (I), and hydroxytrichodesmidane (*ibid.*) with retronecanol (A., 1937, II, 435), $[\alpha]_D -95^{\circ}$. Trichodesmine thus belongs to the *Senecio* group.

E. W. W.

Solubility and hydrogen-ion concentration of quinine salts. I. Effect of the quinine and quinuclidine nitrogens. II. New series of double quinine salts. F. F. JOHNSON (J. Amer. Pharm. Assoc., 1937, 26, 1227—1231, 1231—1233).—I. The $[\text{H}^+]$ of quinine dihydrochloride preps. is const. during sterilisation but increases during storage for 2 years in soft-glass ampoules without pptn. occurring in the prep. Expressions are derived for the degree of hydrolysis of an alkaloid after liberation by dissociation of a salt and for the degree of dissociation of an alkaloidal salt into free acid. The addition of the first equiv. of acid to the quinuclidine-N and of the second to the quinoline-N is confirmed.

II. *Quinine diacetate* and the *acetate*, *propionate*, *valerate*, and *lactate* of quinine hydrochloride were prepared.

F. O. H.

Antiplasmodial action and chemical constitution. I. Cinchona alkaloidal derivatives and allied substances. A. COHEN and H. KING. II. Simple synthetic analogues of quinine and cinchonine. A. D. AINLEY and H. KING (Proc. Roy. Soc., 1938, 125, B, 49—60, 60—92).—I. Antiplasmodial action, i.e., remedial action on canaries infected with *Plasmodium relictum* (= *præcox*), is not very sensitive to stereochemical changes in the cinchona alkaloids (cf. Goodson *et al.*, A., 1930, 1310; Buttle *et al.*, A., 1934, 681), but is lost (generally with an increase in toxicity) when the central $\text{CH}(\text{OH})$ is converted into CHCl , CH_2 , or CH . The following compounds, most of which were tested, are described: quinine chloride [*hydrochloride*, m.p. 219° (decomp.) (previous darkening)]; cinchonine chloride (I) [*hydrobromide*, m.p. 228°]; cinchonidine chloride (II) [*hydrochloride* (+ H_2O), m.p. (anhyd.) 229° (decomp.)]; quinidine chloride (III) [*hydrochloride*, new m.p. 212° (decomp.) (yellow $>200^{\circ}$)]; hydroquinine, hydroquinidine (IV), and hydrocinchonidine [*hydrochloride*, m.p. $233-235^{\circ}$ (decomp.)] chlorides; deoxyquinine [*cuprichloride*, m.p. 178° (decomp.)];

deoxycinchonine, m.p. 91° [*hydrochloride*, m.p. $183-185^{\circ}$ (shrinks at 175°)], and deoxycinchonidine [*hydrochloride*, m.p. $178-180^{\circ}$ (yellow liquid)], obtained by reduction (Fe , dil. H_2SO_4) of (I) and (II), respectively; deoxydihydrocinchonine (+ $2\text{H}_2\text{O}$), m.p. 62° [*hydrochloride*, new m.p. 192° (yellow liquid)], by reduction (H_2 , Pd-C, *n*- H_2SO_4) of (I); deoxydihydroquinidine, by similar reduction of (III) or (IV); deoxydihydrocinchonidine [*hydrochloride*, m.p. $186-188^{\circ}$], by catalytic reduction of (II); quinene [*dihydrochloride*, m.p. $180-185^{\circ}$ (cf. Giemsa *et al.*, A., 1921, i, 583)], hydroquinene [*dihydrochloride* (+ $2\text{H}_2\text{O}$), m.p. $215-218^{\circ}$ (red liquid)], and cinchene [*dihydrochloride* (+ $2\text{H}_2\text{O}$), m.p. $185-190^{\circ}$], prepared from the appropriate chloride and EtOH-KOH.

Methylquitenine [*dihydrochloride* (+ $3\text{H}_2\text{O}$), decomp. $110-120^{\circ}$; *dihydrobromide* (+ $3\text{H}_2\text{O}$), decomp. (anhyd.) 205° (softens $>180^{\circ}$)], which is active (Goodson *et al.*, *loc. cit.*), with conc. aq. NH_3 at 60° and 30% aq. NH_2Me at 50° (pressure) gives *quitenamide* (+ $0.5\text{H}_2\text{O}$), m.p. 203° [*hydrochloride* (+ $2\text{H}_2\text{O}$), m.p. $155-200^{\circ}$, m.p. (anhyd.) 200° (sinters at 197°)], and *quitenmethylanilide* (+ $4\text{H}_2\text{O}$), m.p. 90° , decomp. 100° , resolidifying with m.p. 250° , respectively, both of which are inactive. Methylcinchotenine, new m.p. $250-252^{\circ}$ [*dihydrochloride* (+ H_2O), m.p. about 253° (decomp.)], and *methylcinchotenidine* (+ $2\text{C}_6\text{H}_6$), m.p. (C_6H_6 -free) $152-153^{\circ}$ [*dihydrochloride*, m.p. 235° (decomp.)], are also inactive.

γ -Anilo- α -keto- α -3-pyridylbutane, m.p. $82-83^{\circ}$ (from 3-pyridoylacetone and NH_2Ph at 100°), is converted by conc. H_2SO_4 at 100° into 4,3'-pyridyl-2-methylquinoline, m.p. $108-109^{\circ}$ [*dihydrochloride* (+ $2.25\text{H}_2\text{O}$), m.p. 288° (decomp.)]; *mono*-, m.p. $197-198^{\circ}$, and *di*-, m.p. 205° , *picrate*, and thence by PhCHO into the 2-styryl derivative, m.p. $167-168^{\circ}$; both quinolines are inactive.

II. Since *d*- and *l*-dihydroquinicins (and the *d*-*N*-Me derivative), which are substituted 4-quinolyl-(β -4-piperidylethyl)carbinols, are devoid of antiparasmodial activity, it is possible that such activity is dependent on the close proximity of the piperidine and quinoline rings. The synthesis of 2-piperidyl-4-quinolylcarbinols is accomplished by improved methods (cf. Ruzicka *et al.*, A., 1921, i, 584, 585; 1925, i, 289).

α -Chloro- ϵ -benzamidopentane is successfully prepared from PCl_5 and pure benzpiperidide, b.p. $184-186^{\circ}/17$ mm. (the crude product is freed from partially reduced C_5N_5 derivatives by oxidation with KMnO_4 in COMe_2), and converted by the successive action of aq. EtOH-KCN and EtOH-HCl into Et ϵ -benzamidohexanoate (I), b.p. $204^{\circ}/1$ mm. Cinchoninic acid is obtained by (i) essentially Kaufmann's method (cf. A., 1918, i, 187), (ii) oxidation (KMnO_4 , 50% aq. $\text{C}_5\text{H}_5\text{N}$) of 4-styrylquinoline (from lepidine, PhCHO, and anhyd. ZnCl_2), and (iii) reduction (H_2 , Pd-C, aq. NaOH) of its 2-Cl-derivative; details are given for the prep. of the various intermediates. Et cinchoninate, (I), and NaNH_2 (free from NaNO_2) in C_6H_6 give 64% of 4-quinolyl ϵ -benzamid- α -carbethoxyamyl ketone, hydrolysed by 17% HCl at 100° (bath) to the ϵ -benzamidooamyl, m.p. $113-113.5^{\circ}$, and thence by boiling HCl (const. b.p.) to the ϵ -aminoamyl ketone (II). Br vapour in N_2 converts (II) in 40% HBr at

50° into 4-quinolyl α -bromo- ϵ -aminoamyl ketone dihydrobromide, m.p. 185—186° (decomp.), rapidly converted by shaking with aq. $\text{Na}_2\text{CO}_3 + \text{Et}_2\text{O}$ into 2-piperidyl 4-quinolyl ketone [*dipicrolonate*, m.p. 181—182° (decomp.)], which is (immediately) reduced (H_2 , PtO_2 , MeOH) to 2-piperidyl-4-quinolylcarbinol (III), m.p. 143—144° [sesquisulphate, $2\text{C}_{15}\text{H}_{18}\text{ON}_2 \cdot 3\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, m.p. 172° (decomp.); normal sulphate ($+3\text{H}_2\text{O}$), m.p. 129° (decomp.); mono- ($+ \text{H}_2\text{O}$), m.p. 202° (decomp.), and di- ($+ \text{H}_2\text{O}$), m.p. 230° (decomp.)], -hydrochlorides; *NO*-derivative, m.p. 189° (decomp.). (III) and MeI (1.3 mols.) in COMe_2 (no heat applied) give 2-*N*-methylpiperidyl-4-quinolylcarbinol (IV) [hydrochloride ($+ \text{H}_2\text{O}$), m.p. 138° (decomp.); *dipicrolonate*, m.p. 228° (decomp.); methochloride ($+3.5\text{H}_2\text{O}$), m.p. 168—169° (decomp.); dimethiodide ($+ \text{H}_2\text{O}$), m.p. 244° (decomp.), from (III) and MeI (10 mols.) in boiling MeOH] and its methiodide ($+ \text{H}_2\text{O}$), 2 forms, m.p. 216° (decomp.) and 226—227°. These forms are converted successively into the metho-chloride, -hydroxide, and -hydrosulphide; decomp. of the last at 100°/vac. affords 2 forms of (IV), m.p. 120—121° and 152°, respectively (cf. A., 1925, i, 289), which with MeOH-MeI (1 mol.) regenerate the respective methiodide. (III) and MeI (0.5 mol.) in COMe_2 at room temp. yield (IV) (m.p. 152°) and the hydriodide ($+ \text{H}_2\text{O}$), m.p. 160—161° (decomp.), of (III). An Et_1 derivative of (III) could not be obtained using EtI or EtBr [whereby the hydrobromide ($+ \text{H}_2\text{O}$), m.p. 196—197° (decomp.), is produced]. (IV) and EtI (2 mols.) at 37°/18 days give 2-*N*-ethylpiperidyl-4-quinolylcarbinol methiodide ($+ \text{H}_2\text{O}$), m.p. 114—115°, resolidifying with decomp. 155° (previous softening); ($+2\text{H}_2\text{O}$), decomp. 162—163°, whilst allyl and crotyl iodides (2 mols.) in boiling MeOH and COMe_2 afford 2-*N*-allyl- ($+ \text{H}_2\text{O}$), m.p. 186—186.5° (decomp.), and 2-*N*-crotyl- ($+ \text{H}_2\text{O}$), m.p. 174—175° (decomp.), -piperidyl-4-quinolylcarbinol methiodide, respectively; a little of the di(allyl iodide) ($+1.5\text{H}_2\text{O}$), m.p. 160—161°, of (IV) is also isolable. Allyl iodide and (III) in $\text{COMe}_2 + \text{NaHCO}_3$ at room temp. yield 2-*N*-allylpiperidyl-4-quinolylcarbinol, m.p. 86° [hydriodide ($+ \text{H}_2\text{O}$), m.p. 190—191° (decomp.)], from reactants in boiling MeOH-COMe_2 ; mono- ($+2\text{H}_2\text{O}$), m.p. 87°, and tri- ($+2\text{H}_2\text{O}$), decomp. 180—190° (darkens at 153°), -hydrochloride], which is reduced (H_2 , PtO_2 , MeOH) to 2-*N*-propylpiperidyl-4-quinolylcarbinol, m.p. 100—101° [mono- ($+4\text{H}_2\text{O}$), m.p. 69—70°, and di- ($+3\text{H}_2\text{O}$), m.p. 139—140° (decomp.)], -hydrochlorides], and (III) (by elimination of *N*-substituent). Similarly, 2-*N*-crotyl-, m.p. 89—90° [hydrochloride ($+2\text{H}_2\text{O}$); m.p. 86—87°], gives 2-*N*-butyl-piperidyl-4-quinolylcarbinol [hydrochloride ($+2\text{H}_2\text{O}$), m.p. 100—101°] (which has a close structural resemblance to quinine) and (III).

2-Hydroxy-6-methoxy-4-methylquinoline, new m.p. 268—270° (decomp.) (from *p*- $\text{OMe-C}_6\text{H}_4\text{-NH-CO-CH}_2\text{Ac}$ and conc. H_2SO_4 at $>100^\circ$), and POCl_3 at 130—140° afford the 2-*Cl*-derivative, m.p. 142—144°, reduced (H_2 , Pd-C , AcOH-NaOAc) to 6-methoxy-4-methylquinoline. This yields the 4-styryl derivative, which is oxidised (KMnO_4 , 50% aq. $\text{C}_5\text{H}_5\text{N}$, $<10^\circ$) to 6-methoxyquinoline-4-carboxylic acid (V), also obtained by hydrolysis (60% H_2SO_4) of its nitrile (prep. described; cf. Kaufmann, *loc. cit.*).

The Et ester, b.p. 172°/1 mm., of (V) with (I) and NaNH_2 in C_6H_6 gives 6-methoxy-4-quinolyl ϵ -benzamido- α -carbethoxyamyl ketone, hydrolysed to the ϵ -benzamidoamyl, m.p. 92° [picrate ($+0.5\text{H}_2\text{O}$), m.p. 101—102°, m.p. (anhyd.) 156°], and thence to the ϵ -aminoamyl ketone. 6-Methoxy-4-quinolyl α -bromo- ϵ -aminoamyl ketone dihydrobromide, m.p. 195° (decomp.), is converted by aq. $\text{Na}_2\text{CO}_3 + \text{Et}_2\text{O}$ and subsequent reduction (H_2 , PtO_2 , MeOH) into 2-piperidyl-(6-methoxy-4-quinolyl)carbinol (VI), m.p. 162—163° [mono-, m.p. 221° (decomp.), and di-, m.p. 231—232° (decomp.)], -hydrochlorides], accompanied (in one case) by the stereoisomeric iso-carbinol (VII), m.p. 187—188° [hydrochloride ($+ \text{H}_2\text{O}$), m.p. 206—207° (decomp.)]. (VI) and MeI (0.5 mol.) in COMe_2 at room temp. give 2-*N*-methylpiperidyl-(6-methoxy-4-quinolyl)carbinol, m.p. 183—184° [hydrochloride ($+3\text{H}_2\text{O}$), m.p. 103—104°; methiodide, 2 forms, both m.p. 251°, not convertible through the methohydrosulphide into the carbinol], together with the hydriodide, m.p. 214° (decomp.), of (VI). 2-*N*-Allyl- (VIII), m.p. 136—137° [mono- ($+ \text{H}_2\text{O}$), m.p. 129°, and di-, m.p. 174—175° (decomp.)], -hydrochlorides], and 2-*N*-crotyl-, m.p. 97—98° [mono- ($+2\text{H}_2\text{O}$), m.p. 115—116°, and di-, m.p. 189—190° (decomp.)], -hydrochlorides], -piperidyl-(6-methoxy-4-quinolyl)carbinols, prepared from (VI) and the requisite iodide in COMe_2 , are reduced (H_2 , PtO_2 , MeOH) to (VI) (elimination of *N*-substituent) and the 2-*N*-propyl-, m.p. 153—154° [hydrochloride, m.p. 131°; 1:1 compound, m.p. 135—136°, with (VI)], and 2-*N*-butyl derivative (hydrochloride, m.p. 155—156°), respectively. Solutions of some specimens of crude (VIII) in hot N-HCl deposit 6-methoxy-4-quinolylcarbinol ($+2\text{H}_2\text{O}$), m.p. 83—84° [methiodide, m.p. 245° (decomp.)], also formed as a by-product during the prep. of (VI).

Of all the carbinols tested, only (VI) (more active) and (VII) show antiparasmodial activity. H. B.

Microscopic examination of ergot alkaloids.

IV. Mixed ergot alkaloids. A. KOFLER (Arch. Pharm., 1938, 276, 61—77; cf. A., 1938, II, 117).—All the ergot alkaloids investigated form mol. compounds of a *d*- with any *l*-alkaloid. The m.p. of these compounds is usually lower and sharper than that of the components. The compounds are microscopically very similar and are truly isomorphous, e.g., they form true mixed crystals with each other. Thirteen such compounds are described. Some are obtained from CHCl_3 , C_2HCl_3 , or, less often, C_6H_6 , others from all solvents. Microscopic recognition of mixed ergot alkaloids is thus often extremely difficult; it is sometimes assisted by spontaneous change of one ingredient and by the frequent formation of less sol. solvates, e.g., ergosamine + MeOH . Fifteen photomicrographs are given. R. S. C.

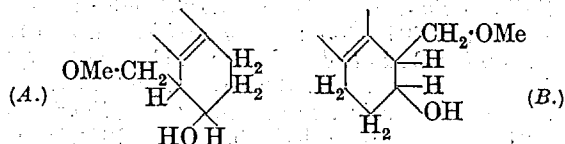
Ergot alkaloids. III. Partial syntheses of ergobasine and of its optical antipode. A. STOLL and A. HOFMANN (Z. physiol. Chem., 1938, 251, 155—163; cf. A., 1938, II, 35).—The partial synthesis of ergobasine (I) (ergometrine) is the first successful prep. of a physiologically active ergot alkaloid from inactive components and the proof that lysergic acid (II), the typical product of the degradation of all the compounds of the series, is the actual component of

the mol. The contracting action on the uterus is proper to the natural alkaloid and not to its optical antipode. Attempts to obtain amide-like derivatives of (II) are unsuccessful by reason of the sensitiveness of (II) to acid. A suitable initial material is *isolysergihydrazide*, readily obtained from *Me lysergate* or, directly, by treatment of the ergot alkaloids with warm $N_2H_4 \cdot H_2O$. This is transformed into *r-isolysergazine*, which with *d*- β -amino-*n*-propyl alcohol gives a mixture (III) of amides separated chromatographically by Al_2O_3 (Brockmann) into *d-isolyserg-d- β '-hydroxyisopropylamide* (IV), m.p. 196° (corr.; decomp.), $[\alpha]_D^{20} +416^\circ$, $[\alpha]_{5461}^{20} +523^\circ$ in $CHCl_3$, identical with natural ergobasine (ergometrinine), and *l-isolyserg-d- β -hydroxyisopropylamide*, $[\alpha]_D^{20} -342^\circ$ in $COMe_2$ [perchlorate, m.p. 212° (corr.; decomp.)]. Treatment of (IV) with $AcOH$ or $EtOH-H_3PO_4$ gives *d-lyserg-d- β -hydroxyisopropylamide* (V), m.p. 159–162° (corr.; decomp.), $[\alpha]_D^{20} +91^\circ$ in H_2O , identical with natural ergobasine. Alternatively (III) is isomerised directly with $EtOH-H_3PO_4$ and (V) is isolated from the product as its tartrate. An analogous series of reactions leads to the isolation of *l-isolyserg-l- β -hydroxyisopropylamide*, m.p. 196° (corr.; decomp.), $[\alpha]_D^{20} -415^\circ$ in $CHCl_3$, isomerised to *l-lyserg-l- β '-hydroxyisopropylamide* (*l-ergobasine*), m.p. 159–162° (corr.; decomp.), $[\alpha]_D^{20} -89^\circ$ in H_2O . H. W.

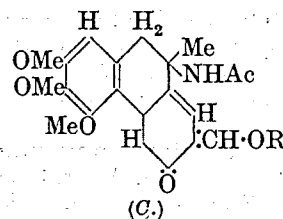
[Ergocristine and ergocristine, alkaloids from ergot.] A. STOLL and E. BURCKHARDT (Z. physiol. Chem., 1938, 254, 287; cf. A., 1938, II, 35).—The alkaloid double compound, ergocristine-ergosinine, appears to have been described by Kofler (cf. A., 1937, II, 393). Preps. consisting essentially of ergocristine or ergocristine have probably been obtained by Barger and Ewins (J.C.S. 1910, 97, 284; 1918, 113, 235). H. W.

Colchicine. K. BURSIA (Ber., 1938, 71, [B], 245–257).—Hydrogenation of colchicine (I) [Pt (Adams–Shriner) in pure $MeOH$] leads to absorption of 7 H, giving (II) and a compound, $C_{22}H_{31}O_5N$, m.p. (from $EtOAc$) 151° after softening at 142° or, after being heated at 110°, m.p. 171°; this is neutral and hence retains $NHAc$. It readily gives a monoacetate, m.p. 210°, and a monobenzoate, m.p. 246°. Titration of it with Br in $CHCl_3$ causes absorption of 2 Br but HBr and a compound, $C_{21}H_{29}O_5NBr$, m.p. 170°, result. Hydrogenation (Pt in $AcOH$) of colchicine (VI) proceeds less uniformly than that of (I), giving *hydrocolchicine*, $C_{21}H_{29}O_6N$, m.p. 202–203° (*diacetate*, m.p. 166°), and (III). Maleic anhydride does not appear to add to (I) or (VI) in boiling C_6H_6 or at 130°. After protracted contact (I) or (VI) absorbs

about 0.5 O from BzO_2H . The close similarity of the absorption spectra of (I) (C ; $R = Me$) and (VI) (C ; $R = H$) in $CHCl_3$ excludes the possibility of the presence of an appreciable amount of the OH-aldehyde form in (VI). In alkaline solution the spectrum of (VI) has two new bands, one of which is due to the NH_4 salt of (VI) whilst the other denotes the presence of the OH-aldehyde form. Ozonisation of (VI) proceeds non-homogeneously and does not yield cryst. derivatives. NH_2Ac is the sole cryst. product of the dehydrogenation of (I) by Se. H. W.



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Tertiary arsines and arsine oxides. F. F. BLICKE and E. L. CATALINE (J. Amer. Chem. Soc., 1938, 60, 419–422).— $(AsPh_2)_2O$, $PhBr$, and $Na-Hg$ give $AsPh_3$ by way of $AsPh_2Na + AsPh_2ONa$, the mechanism being proved by the fact that $Na-Hg$ in air leads to $NaAsPh_2O_2$ (from $AsPh_2Na$ and O_2) and $(AsPh_2)_2O$ (from $AsPh_2ONa$ and H_2O). $AsPhO$ or As_2Ph_4 with $Na-Hg$ and $PhBr$ similarly affords $AsPh_3$. $C_6H_4Br-C_6H_4-AsO_2H$ and $HI-HBr-SO_2$ give 4-bromodiphenyl-4'-bromoarsine, m.p. 45–46°. ($m-NO_2-C_6H_4$) $_3AsO$ and HPO_2-HI give tri-*m*-nitrophenylarsine, m.p. 206–207° (cf. Michaelis, A., 1902, i, 515), reconverted by $KMnO_4$ into the oxide, reduced by $SnCl_2$ in $AcOH$ to tri-*m*-aminophenylarsine (I), m.p. 178–179°, the Ac_3 derivative of which with $KMnO_4$ yields tri-*m*-acetamidophenylarsine dihydroxide, m.p. >300°, hydrolysed by $NaOH$ to tri-*m*-aminophenylarsine oxide, m.p. 272° [giving (I) when reduced]. With HNO_2 this gives tri-*m*-hydroxyphenylarsine oxide, m.p. >300°, and thence tri-*m*-hydroxyphenylarsine, m.p. 187–188° (Me_2 ether, m.p. 112–113°, also prepared from $OMe-C_6H_4-MgI$ and $AsCl_3$). *p*- $OMe-C_6H_4-MgI$ and $AsCl_3$ give tri-*p*-anisylarsine, m.p. 157–159°, converted into the dihydroxide, m.p. 92–94°, which is also obtained from tri-*p*-hydroxyphenylarsine oxide (II), m.p. 276–278° (decomp.). (*p*- $NHAc-C_6H_4$) $_3As$ by oxidation and hydrolysis yields tri-*p*-aminophenylarsine oxide, m.p. >300°, converted

into (II) by HNO_2 . The following are prepared from a diarylhalogenoarsine and a Grignard reagent. Diphenylmethyl-, b.p. 186—188°/21 mm. (HgCl_2 additive compound, m.p. 188°/189°; dihydroxide, m.p. 154—155°), diphenylcyclohexyl-, b.p. 200—203°/4 mm. (HgCl_2 additive compound, m.p. 233—234°; dihydroxide, m.p. 206—207°), 4-bromotriphenyl-, m.p. 64—65° (HgCl_2 additive compound, m.p. 175—176°; dihydroxide, m.p. 180—181°), phenyldi- α -naphthyl-, m.p. 205—206° (dihydroxide, m.p. 242—243°), diphenyl- α -naphthyl-, m.p. 110—111° (HgCl_2 additive compound, m.p. 235—236°; dihydroxide, m.p. 190—191°), diphenyl- β -naphthyl-, m.p. 90—91° (HgCl_2 additive compound, m.p. 200—201°), phenyl-2 : 2'-diphenyl-, m.p. 87—88° (HgCl_2 additive compound, m.p. 204—205°; dihydroxide, m.p. 107—108°), *p*-anisyl-2 : 2'-diphenyl-, m.p. 115—116° (HgCl_2 additive compound, m.p. 196—197°), and α -naphthyl-2 : 2'-diphenyl-arsine, m.p. 150—151° (dihydroxide, m.p. 212—213°), 10-methyl-, b.p. 192—195°/16 mm. (dihydroxide, m.p. 149—151°), 10-phenyl-, m.p. 108—109° (HgCl_2 additive compound, m.p. 201—202°; dihydroxide, m.p. 188—189°), and 10- α -naphthyl-phenox-arsine, m.p. 137—138° (dihydroxide, m.p. 191—192°), and tri-*p*-anisylarsine oxide, m.p. 92—94°.

R. S. C.

Arsonium compounds. F. F. BLICKE and E. L. CATALINE (J. Amer. Chem. Soc., 1938, 60, 423—424).—From a *tert.* arsine oxide and a Grignard reagent are prepared diphenylmethylcyclohexyl-, m.p. 220—221°, triphenylmethyl-, m.p. 175—176°, diphenyl- α -naphthylmethyl-, m.p. 190—191°, phenyl-2 : 2'-diphenylmethyl-, m.p. 117—118°, 10-phenyl-10-methyl-phenox-, m.p. 170—171°, and 10- α -naphthyl-10-methyl-phenox-arsonium iodide, m.p. 143—144°, triphenylcyclohexyl-, m.p. 183—184°, diphenyl-2 : 2'-diphenyl-, m.p. 240—241°, and 10 : 10-diphenylphenox-arsonium bromide, m.p. 229—230°. AsPh_4Cl with Ag_2CO_3 in H_2O gives tetraphenylarsonium *H* carbonate, m.p. 173—174° (decomp.), with picric acid gives the *picrate*, m.p. 203—204°, and with Ag_2O the hydroxide, which affords the *nitrate*, m.p. 260—262°, *sulphate*, m.p. 257—258°, and *acetate*, m.p. 215—217°. At 315—335° AsPh_3RBr (R = Me, Ph, or cyclohexyl) gives AsPh_3 and RBr.

R. S. C.

Exchange reactions of halides of 10-chloro-9 : 10-dihydrophenarsazine and certain magnesium organic halides. V. V. SCHTISCHEVSKI and A. I. VORONINA (J. Gen. Chem. Russ., 1937, 7, 2406—2409).—10-Chloro-9 : 10-dihydrophenarsazine reacts with a no. of Grignard compounds [$(\text{C}:\text{MgI})_2$, $(\text{C}:\text{MgBr})_2$, $(\text{CH}:\text{MgBr})_2$, $(\text{CMe}_2:\text{MgBr})_2$] to yield 10-iodo-, m.p. 218°, or 10-bromo-9 : 10-dihydrophenarsazine, m.p. 212—213°.

R. T.

Cadmium diphenyl. A. N. NESMEJANOV and L. G. MAKAROVA (J. Gen. Chem. Russ., 1937, 7, 2649—2653).—LiPh in Et_2O and CdBr_2 in a N_2 atm. yield Cd diphenyl, m.p. 173—174° (readily decomposed by O_2 or H_2O), which in Et_2O gives HgPh_2 with HgCl_2 , SnPh_4 with SnCl_4 , SbPh_3 with SbCl_3 ; with HCl , H_2O , EtOH , NH_2Ph , NH_3 , C_2H_2 ,

or fluorene it gives C_6H_6 , and, with N_2O_3 in CHCl_3 , $\text{PhN}_2\cdot\text{NO}_3$. It does not react with CHCl_3 (12 hr. at 100°).

R. T.

Organic mercury derivatives. II. Analysis of water-soluble organic mercury compounds. III. Reaction of mercury dialkyl with mercury salts of dibasic acids. IV. Electrochemical symmetrisation of mixed mercury organic compounds. N. N. MELNIKOV and M. S. ROKITZKAJA (J. Gen. Chem. Russ., 1937, 7, 2383—2384, 2518—2522, 2596—2599).—II. H_2O -sol. org. Hg compounds may be titrated with standard KCNS, in presence of Fe^{III} .

III. The reaction $\text{HgR}_2 + \text{HgA} \rightarrow (\text{HgR})_2\text{A}$ (R = alkyl, A = dibasic acid radical), takes place at 100—120°. The following salts were thus prepared: $(\text{HgR})_2\text{SO}_4$ (R = Et, Pr^a , Bu^a , *isoamyl*, decomp. at 188°), and $(\text{CH}_2\text{CO}_2\text{HgR})_2$ (R = Et, m.p. 157—158°, Pr^a , m.p. 133—134°, Bu^a , m.p. 123—124°, *isoamyl*, m.p. 133—134°, Ph, m.p. 215°). HgEt_2 and Hg butyrate or *isovalerate* yield *HgEt butyrate*, b.p. 170—171°, or *isovalerate*, m.p. 24°, b.p. 171—174°/15 mm.

IV. Electrolysis of aq. solutions of salts of the type HgRX (R = Me, Et, Pr^a , Bu^a , *isoamyl*; X = HSO_4 , $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2$) gives HgR_2 , Hg, and X_2 .

R. T.

Mercury derivatives of diphenyl. F. B. HULL (J. Amer. Chem. Soc., 1938, 60, 321—322).—Cu converts the HgCl_2 double salts of the appropriate diazonium compounds into diphenyl-4 : 4'-dimercurichloride, m.p. 286—>335° (decomp. from 230°), -4-, m.p. 328° (decomp. at 325°), and -2-mercurichloride, (I), m.p. 169° (*acetate*, m.p. 109.5°; *nitrate*, m.p. 156.2°; *picrate*, sinters at 57—99°). With 3 mols. of KCN in EtOH (I) gives *bis*-2-diphenylmercury, m.p. 168°, converted by Hg butyrate in EtOH into diphenyl-2-mercuributyrate, m.p. 91.2°.

Effect of various factors on the formation of ammonia by boiling proteins with potash.—See A., 1938, II, 202.

Alkalinity of the ash and loss of chloride during ashing.—See A., 1938, III, 362.

Micro-mol. wt. determinations.—See A., 1938, I, 216.

Determination of carbon and hydrogen. H. STERNBERG (Mikrochim., 1938, 24, 65—95).—A review.

Automatic analysis for elements.—See A., 1938, I, 217.

Micro-determination of halogens and sulphur by Carius' method.—See A., 1938, I, 211.

Colorimetric determination of fructose.—See A., 1938, III, 361.

Standardisation of 2 : 6-dichlorophenol-indophenol.—See A., 1938, III, 217.

Standardization of the dye used for the determination of vitamin-C.—See A., 1938, III, 217.

Determination of amino-acids.—See A., 1938, III, 361.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MAY, 1938.

Methods of writing chemical formulæ and representing the course of reactions. B. EISTERT (Ber., 1938, 71, [B], 237—240).—The proposed method is a combination of those of Robinson and Baumgarten.

H. W.

Oxidation of methane [and other hydrocarbons]. H. FUJIMOTO (Bull. Chem. Soc. Japan, 1938, 13, 281—291).—Passage of a hydrocarbon and O_2 through a silent discharge at 0.06 amp. and 13,000 v. causes change of CH_3R into $(OH\cdot CHR\cdot O)_2$. Thus, CH_4 gives 21.7% of CO_2 and CO and 78.3% of a liquid, from which about 12% of hydroxymethyl peroxide, $(OH\cdot CH_2\cdot O)_2$, m.p. 62° , was isolated. The peroxide is stable at room temp., but explodes when heated; it oxidises KI, $p\text{-}C_6H_4(OH)_2$, and $TiSO_4$, but reduces indigotin. When decomposed, it gives (a) $HCO_2H + H_2$, (b) $2CH_2O + H_2O_2$, and (c) $HCO_2Me + H_2O_2$; heating gives (a) and a little (b); NaOH gives almost entirely (a); Fe, Cu, Zn, Ni, and Pt, but not Al or Cr, act catalytically, giving much (b) and (a) and some (c); MeOH is also formed. By reaction with NH_3 $N(CH_2\cdot O\cdot O\cdot CH_2)_3N$ is formed. C_2H_6 gives similarly $(OH\cdot CHMe\cdot O)_2$ (I), which by thermal decomp. yields (a) $CH_2O + MeCHO + MeO_2H$, (b) $HCO_2Et + MeO_2H$, and (c) much H_2O and H_2 and some CO, CO_2 , and HCO_2H . C_4H_{10} gives *hydroxybutyl peroxide*, b.p. $55\text{--}60^\circ/2$ mm. C_2H_4 gives (I), the reaction being formulated as: $2C_2H_4 + 2O_2 \rightarrow$ (I). A mechanism for the reaction with CH_4 is postulated.

R. S. C.

Ozonisation of hydrocarbons. E. BRINER, C. EL-DJABRI, and H. PAILLARD (Arch. Sci. phys. nat., 1937, [v], 19, Suppl., 154—156).—Oxidation of $n\text{-}C_6H_{14}$, $n\text{-}C_7H_{16}$, $n\text{-}C_8H_{18}$, γ -methylheptane, and $CHMePr^{\beta}_2$ by O_3 is greatly accelerated by small amounts of O_3 at $200\text{--}400^\circ$. Yields of oxidation products are smallest from $CHMePr^{\beta}_2$.

J. D. R.

Catalytic hydrogenation of ethylene on copper-silver alloys.—See A., 1938, I, 259.

Polymerisation of ethylene and acetylene photosensitised by ethyl iodide.—See A., 1938, I, 261.

Ethylenic isomerism of γ -methyl- Δ^{β} -pentene, Δ^{β} -hexene, and δ -methyl- Δ^{β} -pentene. H. VAN RISSEGHEM (Bull. Soc. chim. Belg., 1938, 47, 47—58).—The fraction, b.p. $65.1\text{--}65.7^\circ$, of the product obtained from $CMeEt_2\cdot OH$ by $p\text{-}C_6H_4Me\cdot SO_3H$ (I) is labile and autoxidisable; further purification of the other fractions gives a mixture, b.p. $67.2\text{--}67.8^\circ$, shown by its Raman spectrum to contain $CH_2\text{:}CET_2$, and fractions, b.p. $68.8\text{--}69.4^\circ$ and $70.2\text{--}70.5^\circ$, which

give only one line (1673 cm.^{-1}) in the Raman spectrum and of which the latter is probably $CHMe\text{:}CMeEt$. By means of Raman spectra it is shown that hexan- β -ol with (I) gives a stable mixture, b.p. $68.2\text{--}68.3^\circ$, of about equal parts of *cis*- and *trans*- Δ^{β} -hexene, and with Al_2O_3 gives a mixture containing 30% of the *cis*-form, but that semi-reduction (H_2 -colloidal Pd) of Δ^{β} -hexinene gives pure *cis*- Δ^{β} -hexene, b.p. $68.5\text{--}69.5^\circ$. It is similarly proved that the fractions obtained from $CHMe\text{:}CHPr^{\beta}$ by Al_2O_3 are (a) b.p. $55.3\text{--}55.6^\circ$, a mixture of δ -methyl- Δ^{α} - and *cis*- Δ^{β} -pentene, (b) b.p. $57.6\text{--}57.8^\circ$, a mixture of *cis*- and *trans*- δ -methyl- Δ^{β} -pentene, and (c) b.p. $58.2\text{--}58.6^\circ$, *trans*- δ -methyl- Δ^{β} -pentene. Differences in products obtained by different reagents from various alcohols are compared.

R. S. C.

Preparation of active iron and its application to the semi-hydrogenation of acetylene derivatives.—See A., 1938, I, 258.

Alkylacetylenes and their addition compounds. XXIV. Catalytic hydration of alkylacetylenes.

R. J. THOMAS, K. N. CAMPBELL, and G. F. HENNION (J. Amer. Chem. Soc., 1938, 60, 718—720).—Higher alkylacetylenes are too insol. in H_2O to be hydrated therein by $HgSO_4\text{--}H_2SO_4$, but in 60% AcOH, 70% MeOH, or 70% $COMe_2$ $CBu\text{:}CH$, $C_5H_{11}\text{:}C\text{:}CH$, and $C_6H_{13}\text{:}C\text{:}CH$ give 63—91% yields of hexan-, heptan-, and octan- β -one.

R. S. C.

Formation of free radicals by interaction of sodium vapour with organic halides.—See A., 1938, I, 265.

Periodicity law. P. PETRENKO-KRITSCHENKO (Compt. rend. Acad. Sci. U.R.S.S., 1938, 18, 95—96; cf. A., 1934, I000).—A further statement of the author's views, supported by data for the activities, in EtOH at $<100^\circ$, chiefly of mono-, di-, and tri-substituted halogen derivatives of CH_4 , AcOH, or PhMe.

I. McA.

Explosion of chloroform with alkali metals.—See A., 1938, I, 262.

Reaction products and mechanism in the electrolytic reduction of ethyl iodide. R. E. PLUMP and L. P. HAMMETT (Trans. Electrochem. Soc., 1938, 73, Preprint 10, 149—163).—The electrolytic reduction of EtI in aq. EtOH in a cell with a parchment-paper diaphragm yields H_2 , C_2H_4 , C_2H_6 , and C_4H_{10} in proportions which vary with the p_H of the solution and the nature of the cathode. The results can be explained on the assumption that Et is first formed, and then reacts with H_2 or with itself. The catalytic activity of metals for this reaction is almost the same

as for formation of H_2 . Reduction of EtI by Zn , $Zn-Hg$, and $Zn-Cu$ couple is similar to the electrolytic reduction when electrolytes are present. J. W. S.

Action of magnesium on $\omega\omega'$ -dihalogeno-paraffins. $\alpha\epsilon$ -Dibromododecane from $\alpha\epsilon$ -dibromohexane. $\alpha\epsilon$ -Dibromotetradecane from $\alpha\gamma$ -dibromoheptane. A. MÜLLER and A. F. SCHÜTZ (Ber., 1938, 71, [B], 689—691).— Mg (1 atom) is dissolved in $Br[CH_2]_6\cdot Br$ (4—5 mols.) in Et_2O at -14° ; Et_2O is replaced by $PhMe$ or light petroleum and the mixture is heated at 120° for 6 hr., whereby $Br[CH_2]_{12}\cdot Br$ is obtained in about 30% yield (calc. on the $Br[CH_2]_6\cdot Br$ used). Excess of $Br[CH_2]_6\cdot Br$ is recovered unchanged. $I[CH_2]_6\cdot I$ gives poorer yields of $I[CH_2]_{12}\cdot I$. Mg dissolves less readily in $Br[CH_2]_{12}\cdot Br$ than in $Br[CH_2]_6\cdot Br$ and the yield of $Br[CH_2]_{14}\cdot Br$ is about 26%. Under similar conditions $Br[CH_2]_{10}\cdot Br$ reacts very slowly with Mg ; it is not possible to extract $Br[CH_2]_{20}\cdot Br$ from the products of the change at room temp. or 35° . Replacement of Mg by Na or Li leads to mixtures from which individual compounds cannot be isolated.

H. W.

Decomposition of alcohols by mixed catalysts.—See A., 1938, I, 259.

Gauthier's reaction of synthesis of *tert.*- α -keto-alcohols. A. M. CHALETZKI (J. Gen. Chem. Russ., 1937, 7, 2854—2856).— $MgBu^iCl$ or $MgEtCl$ reacts with ketone cyanohydrins to yield *tert.* alcohols; α -keto-alcohols are not formed. The following are probably new: $\alpha\beta\beta$ -trimethylbutan- β -ol, m.p. 83—84°, $\beta\beta\gamma$ -trimethylpentan- γ -ol, b.p. 152—155°, and γ -methylhexan- γ -ol, b.p. 60°/26 mm.

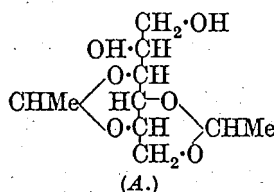
R. T.

l-Gulomethylitol. H. MÜLLER and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 251—262).—*l*-Xylose is converted by H_2SO_4 -anhyd. $CuSO_4$ in $COMe_2$ into 1:2:3:5-diisopropylidenexylose, m.p. 43—45° (corr.), partly hydrolysed by 0.16% HCl at room temp. to 1:2-isopropylidene-*l*-xylose, b.p. 138°/0.3 mm., which gives very hygroscopic crystals. It is transformed by p - $C_6H_4Me\cdot SO_2Cl$ in $C_5H_5N\cdot CHCl_3$ into 1:2-isopropylidene-*l*-xylose 5-*p*-toluenesulphonate, m.p. 137—138° (corr.), which with NaI in $COMe_2$ at 100° gives 5-iodo-1:2-isopropylidene-*l*-xylomethylitol, m.p. 106—109°, transformed by H_2 -Raney Ni into 1:2-isopropylidene-5-*l*-xylomethylitol (I), m.p. 70°, whence *l*-xylomethylitol. Hydrolysis of (I) with 1% H_2SO_4 followed by addition of $BaCO_3$ and treatment with HCl and $Ba(OH)_2$ affords *l*-gulomethylonolactone (III), m.p. 181—182° (corr.), reduced by $Na-Hg$ to (not isolated) *l*-gulomethylitol (III), $[\alpha]_D^{25} +40.8^\circ \pm 1.5^\circ$ in H_2O [*p*-bromophenylhydrazone, m.p. 136° (corr.); phenylosazone, m.p. 183—184° (corr.)]. (III) is hydro-

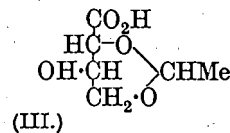
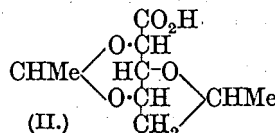
genated (Raney Ni ; 100° or $135^\circ/100$ atm.) to *l*-gulomethylitol (IV), m.p. 131—132° (corr.), $[\alpha]_D^{25} +3.97^\circ \pm 0.5^\circ$ in H_2O , $[\alpha]_D^{25} +16.71^\circ \pm 0.9^\circ$ in saturated borax. The mother-liquors from (III) yield a brucine salt, m.p. 165—168° (corr.), the acid from which gives mainly a non-cryst. lactone. The small amount of cryst. lactone, $C_6H_{10}O_5$, m.p. 130—131° (corr.), has increasing mutarotation, $[\alpha]_D^{25} +31.8^\circ \pm 1.5^\circ$ to $+50.7^\circ \pm 1.5^\circ$ in H_2O . The acid gives a cryst. double salt,

$C_{12}H_{22}O_{12}Cd_2Br_2\cdot 3H_2O$, $[\alpha]_D^{25} +4.17^\circ \pm 0.5^\circ$ in H_2O , $-5.14^\circ \pm 0.5^\circ$ in 0.1N- HCl , from which only a non-cryst. lactone could be regenerated. H. W.

Diethylidene-*l*-sorbitol, diethylidene-*l*-xylonic acid, ethylidene-*l*-threonic acid, and a new synthesis of *l*-sorbose. K. GÄRTZ and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 186—195).—Contrary to Appel (A., 1935, 734) the structure A is



assigned to diethylidene-*l*-sorbitol (I). According to the amount of $KMnO_4$ used oxidation of (I) gives mainly diethylidene-*l*-xylonic acid (II), m.p. about 255° when rapidly heated after softening at 220° , $[\alpha]_D^{25} -29.4^\circ \pm 1^\circ$ in H_2O , $[\alpha]_D^{25} -5.7^\circ \pm 0.5^\circ$ in $MeOH$ (*Me* ester, m.p. 162—164°, $[\alpha]_D^{25} -17.3^\circ \pm 1.5^\circ$ in $MeOH$), or ethylidene-*l*-threonic acid (III), m.p. 175—176° (corr.), $[\alpha]_D^{25} +55.7^\circ \pm 1^\circ$ in H_2O , $[\alpha]_D^{25} +47.4^\circ \pm 1^\circ$ in $MeOH$ (*Me* ester, m.p. 141—142°, $[\alpha]_D^{25} +48.2^\circ \pm 1^\circ$ in $MeOH$). (II) is oxidised to (III)



by $KMnO_4$. (III) is transformed by 10% $AcOH$ at 100° into *l*-threonolactone, b.p. 146—148°/0.1 mm., identified as the phenylhydrazide, m.p. 161—162°. Treatment of (II) with $SOCl_2\cdot CHCl_3$ gives diethylidene-*l*-xylonyl chloride (II), m.p. 132—138° (corr.); this is converted by CH_2N_2 into the non-cryst. diazoketone, transformed by 1% H_2SO_4 at 100° into *l*-sorbose. Reaction does not appear to occur between (IV) and HCl in $C_6H_6\cdot Et_2O$. With $AgCN$ in $CHCl_3$ and subsequently at 115 — 120° (IV) gives a product, $C_9H_{14}O_6$, m.p. 253—255° when rapidly heated, and a compound, m.p. 118—121°, which may be diethylidene-*l*-xylose. Attempts to prepare this substance according to Appel (*loc. cit.*) gave a very unstable product readily undergoing a complex polymerisation to a compound, $C_9H_{14}O_5$, m.p. 202—203° (decomp.).

H. W.

Crystalline lactositol. M. L. WOLFROM, W. J. BURKE, K. R. BROWN, and R. S. ROSE, jun. (J. Amer. Chem. Soc., 1938, 60, 571—573).—Hydrogenation of lactose (400 g.) in H_2O (600 g.) at p_H 3.4 in presence of Ni at 143—150°/138—128 atm. gives lactositol, m.p. 146°, $[\alpha]_D^{25} +14^\circ$ in H_2O (no hydrate); *CPh_3* ether hexaacetate, m.p. 249—251°, $[\alpha]_D^{27} -40.1^\circ$ in $CHCl_3$, for the hydrolysis of which $k \times 10^3$ (unimol.) = 0.873 at 60° and 4.00 at 70° , whence the energy of activation = 33,600 g.-cal. A pyranoside structure is indicated.

R. S. C.

Preparation of absolute ether. W. F. BRUCE (Science, 1938, 87, 171—172).—450 g. of technical flake $NaOH$ and 3000 ml. of Et_2O are kept at 25—30° for 2 weeks, with occasional shaking. The Et_2O should then be colourless and may be used, without distillation, for Grignard reactions etc. It is best stored over Na in bottles < three quarters full; no peroxide is formed under these conditions.

L. S. T.

Ether-like compounds. XX. Preparation of monoethers of tetramethylene glycol. M. H. PALOMAA and A. A. ERIKOSKI (Ber., 1938, 71, [B], 574—575).—Mg covered with pure Et_2O (the quality is very important) is treated with a little EtBr and then gradually with $\text{COMe} \cdot [\text{CH}_2]_3 \cdot \text{Cl}$. When reaction is complete the excess of Et_2O is removed by distillation. C_6H_6 followed by trioxymethylene is added, and the mixture is heated for $\frac{1}{2}$ — $\frac{1}{2}$ hr. The product is decomposed with dil. H_2SO_4 and extracted with C_6H_6 . Tetramethylene glycol Me_1 ether, b.p. 63 — $64^\circ/7$ mm., $171^\circ/745$ mm., is obtained in 54% yield. H. W.

Raman spectra of sodium ethyl sulphonates and sulphinates.—See A., 1938, I, 229.

Preparations and reactions of di- β -chloroethyl sulphate. C. M. SUTER and P. B. EVANS (J. Amer. Chem. Soc., 1938, 60, 536—537).—Addition of SO_3 (1 mol.) to $(\text{Cl} \cdot [\text{CH}_2]_2)_2\text{O}$ (I) and distillation within 2—3 hr. gives a good yield of $(\text{Cl} \cdot [\text{CH}_2]_2)_2\text{SO}_4$ (II), b.p. 126 — $129^\circ/3$ mm., probably by way of an adduct with SO_3 ; longer keeping reduces the yield; heating at 150° and washing with H_2O prior to distilling gives only a 30% yield. With hot H_2O (II) gives quantitatively $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{OH}$ and HCl , one alkyl only reacting. Conc. HCl similarly gives $(\text{CH}_2\text{Cl})_2$, but gaseous HCl is without effect. Reaction with Bu^+OH is complex, $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{OH}$ and (I), but no $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{OBu}^+$, being formed. With hot AcOH (II) slowly, and with hot $\text{NaOAc} \cdot \text{AcOH}$ rapidly, gives $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{OAc}$; with aq. NaOBz it gives a little and with dry NaOBz at 170° 62% of $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{OBz}$. $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{SBz}$ is obtained in 61% yield. With MgPhBr (II) gives slowly 25% of $\text{CH}_2\text{Ph} \cdot \text{CH}_2\text{Cl}$ and $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{Br}$, and with $\text{CH}_2\text{Ph} \cdot \text{MgCl}$ rapidly 66% of $\text{Ph} \cdot [\text{CH}_2]_3 \cdot \text{Cl}$. One alkyl reacts with NaOPh yielding $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{OPh}$. Reaction with $\text{CHNa}(\text{CO}_2\text{Et})_2$ is rapid, but gives no pure products. $(\text{Br} \cdot [\text{CH}_2]_2)_2\text{O}$ and SO_3 give a poor yield of the sulphate. Pr^+O and $(\text{Cl} \cdot [\text{CH}_2]_2)_2\text{O}$ give tars. R. S. C.

Mechanism of ester condensation. S. ESKOLA (Suomen Kem., 1938, 11, A, 15—19).—An historical review of theories of the Claisen and similar condensations. M. H. M. A.

Existence of labile molecules as constituent elements of organic acids and of organic compounds in general. A. MIOLATI (Mem. R. Accad. Ital., 1937, 8, 215—241).—Theoretical. A review of the literature on the biochemical oxidation and the electrolysis of AcOH and related acids, and on common naturally occurring acids, suggests the existence of labile mols., such as $\text{CH} \cdot \text{CO}_2\text{H}$, capable of polymerisation. E. W. W.

Dehydration of glacial acetic acid. S. KILPI (Suomen Kem., 1938, 11, B, 7).—Glacial AcOH is distilled over P_2O_5 and the Ac_2O formed determined by addition of excess of an amine and back titration with HClO_4 potentiometrically. The Ac_2O is removed by heating for 12 hr. near the b.p. with the theoretical amount of H_2O . M. H. M. A.

Exchange reactions of acetic acid and acetate ions in heavy water. L. D. C. BOK and K. H. GEIB (Naturwiss., 1938, 26, 122).—The exchange of

H attached to C in acetates and AcOH with D of D_2O , and the reverse, has been investigated. In KOAc solutions the exchange was not affected by $[\text{KOAc}]$, so the exchange must take place between OAc^- and H_2O . Addition of OH^- catalyses the exchange $\propto [\text{OH}^-]$. The exchange with undissociated AcOH is catalysed by H^+ . A. J. M.

Rate of hydrolysis of methyl di- and tri-chloroacetate.—See A., 1938, I, 256.

Three isomeric pentinoic acids. E. SCHJÄNBERG (Ber., 1938, 71, [B], 569—573).— Δ^2 -Pentenoic acid is converted by Br in CS_2 in diffused daylight at 0° into γ -8-dibromovaleric acid, m.p. 56.5° , transformed by boiling $\text{KOH} \cdot \text{EtOH}$ into Δ^2 -pentinoic acid, m.p. 57.5° , which with Cu_2O followed by $\text{K}_3\text{Fe}(\text{CN})_6$ in presence of alkali appears to yield the acid, $(\text{C} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2$, decomp. 50° . $\beta\gamma$ -Dibromovaleric acid, m.p. 64.5° , and $\text{KOH} \cdot \text{EtOH}$ yield the corresponding $\beta\gamma$ - $(\text{OH})_2$ and γ -CO-acid with a mixture of bromopentenoic acids and Δ^2 -pentinoic acid, b.p. $80^\circ/1$ mm., m.p. 52.2° . Δ^2 -Pentenoic acid and Br in CS_2 slowly yield $\alpha\beta$ -dibromovaleric acid, m.p. 57.0° , which with $\text{KOH} \cdot \text{EtOH}$ gives β -bromo- Δ^2 -pentenoic acid, m.p. 53.0° . Further treatment of this with KOH gives COMeEt , apparently formed thus: $\text{C} \cdot \text{EtBr} \cdot \text{CH} \cdot \text{CO}_2\text{H} \rightarrow \text{C} \cdot \text{Et} \cdot \text{C} \cdot \text{CO}_2\text{H} \rightarrow \text{COMeEt}$. CMeEtCl_2 is transformed by $\text{KOH} \cdot \text{EtOH}$ at 130 — 135° into a mixture of $\text{C} \cdot \text{Et} \cdot \text{CH}$ and C_2Me_2 . These are transformed by Na into $\text{C} \cdot \text{Et} \cdot \text{CNa}$, which with CO_2 and Et_2O affords Δ^2 -pentinoic acid, b.p. $104^\circ/10$ mm., m.p. 49.0° . H. W.

Dehydration products of lactic acid as a type of the transformations of cyclic esters into linear polyesters. S. BEZZI, L. RICCIBONI, and C. SULLAM (Mem. R. Accad. Ital., 1937, 8, 127—213).—The anhydro-polymerides of lactic acid (I), viz., $\text{OH} \cdot [\text{CHMe} \cdot \text{CO}_2]_n \cdot \text{H}$ and $\text{OH} \cdot [\text{CHMe} \cdot \text{CO}_2]_n \cdot \text{H}$, previously known as lactyl- and polylactyl-lactic acids, are renamed *dilactylic acid* (II) and *polylactylic acids* (III). The dissociation const., K , of (I) is determined as 0.23×10^{-3} , and that of (II) as 1.11×10^{-3} , both in H_2O (quinhydrone electrode), and as 1.04×10^{-5} and 5.17×10^{-5} , respectively, in 50% EtOH (H_2 electrode). The (III) obtained by heating (I) at 120° have K practically equal to that of (II). The velocity of hydrolysis of lactide (IV) to (I) is determined at varying temp. and $[\text{HCl}]$, and energy of activation (q) and activity coeff. (α) are calc. for H^+ and for H_2O , at 0 — 70° . Hydrolysis of (II) to (I) is also studied, and q and α are calc. From the rates of hydrolysis of (III) in aq. COMe_2 , first and second velocity coeffs., k_1 and k_2 , are determined, and various formulæ are considered (cf. Kuhn, A., 1932, 576). For (III) of mol. wt. 1310, 16 linkings are hydrolysed with k_1 , and one with k_2 [practically equal to that for (II)]; $k_2/k_1 = 10.8$ at 60° , 13.1 at 70° (cf. cellulose; A., 1936, 57). The (III) formed by heating (I) at 80 — 120° at atm. pressure are shown by k of hydrolysis not to be accompanied by (IV), which is therefore thought not to be an intermediate in the formation of (III). Conversion of (IV) at 145° into (III) is studied, and ascribed to the intermediate formation of (II) and H_2O ; (II) is regarded as the only precursor of (III), contrary to the view of Carothers (A., 1936,

295, etc.). The various equilibria involved are discussed. E. W. W.

Alkylation of ethyl acetoacetate in an aqueous medium. I. L. KNUNIANZ (J. Gen. Chem. Russ., 1937, 7, 2852—2853).— $\text{CHMeAc}\cdot\text{CO}_2\text{Et}$ is obtained in 98% yield from $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ in 20% KOH and Me_2SO_4 at $<40^\circ$. R. T.

Condensation of ω -hydroxyundecic acid.—See A., 1938, I, 257.

Wool wax. I. Lanopalmitic acid. T. KUWATA (J. Amer. Chem. Soc., 1938, 60, 559—560).—Lanopalmitic acid (modified prep. from merino wool), m.p. $86\text{--}87^\circ$, $[\alpha]_D^{25} -1^\circ$ in EtOH (*Mg* salt, m.p. $>280^\circ$), is proved to be *l*- α -hydroxypalmitic acid. With PbO_2 it gives $n\text{-C}_{14}\text{H}_{29}\text{CHO}$. Its *Me* ester, b.p. $230\text{--}231^\circ/5\text{ mm.}$, m.p. $45\text{--}46^\circ$, $[\alpha]_D^{25} -1.5^\circ$ in EtOH, is oxidised by CrO_3 in AcOH to *Me* lanopalminonate (α -keto-palmitate) (I), m.p. $47\text{--}47.5^\circ$, the acid, m.p. 69° , from which with 30% H_2O_2 gives $n\text{-C}_{14}\text{H}_{29}\text{CO}_2\text{H}$, also obtained from the oxime, m.p. 92° , of (I) by PCl_5 , followed by HCl at $150\text{--}160^\circ$, by way of $n\text{-C}_{14}\text{H}_{29}\text{CO}\cdot\text{NH}_2$. *dl*- $\text{C}_{14}\text{H}_{29}\text{CHBr}\cdot\text{CO}_2\text{H}$ yields *Me* *dl*- α -hydroxypalmitate, m.p. $58\text{--}59^\circ$, which with CrO_3 gives (I). R. S. C.

Constitution of the inner condensation product of dimethyl α -tanacetonedicarboxylate. S. RANTA (Suomen Kem., 1938, 11, B, 8—9).—By heating a 4% solution of β -tanacetonedicarboxylic acid, m.p. $117\text{--}119^\circ$, an acid, $\text{C}_9\text{H}_{14}\text{O}_4$, m.p. $155\text{--}156^\circ$ (*Me*₂ ester, b.p. $142^\circ/14\text{ mm.}$), is obtained. This acid is oxidised (KMnO_4) to $\text{H}_2\text{C}_2\text{O}_4$ and γ -keto- δ -methyl-*n*-hexoic acid. The acids of m.p. 119° and 156° are *cis*- and *trans*-forms, but the constitution is not decided. F. R. S.

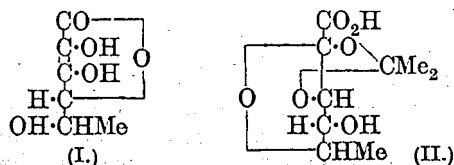
Reaction of ethyl dihydroxymalonate and its application to the detection of mesoxalic acid. J. PARROD (Compt. rend., 1938, 206, 355—357).— $\text{C}(\text{OH})_2(\text{CO}_2\text{Et})_2$ (I) [from $\text{CH}_2(\text{CO}_2\text{Et})_2$ and NO_2] when heated with aq. ZnSO_4 and NH_3 gives a rose colour changing to brown. Exposure to light gives an intense green fluorescence by which one part of (I) in 2000 may be detected. Presence of Zn is essential. NH_3 alone or with CdSO_4 gives a yellowish colour. Presence of Ni^{++} or Co^{++} or replacement of NH_3 by amines inhibits the reaction. In presence of Cu^{II} salts (I) decomposes giving CuCN . $\text{CO}(\text{CO}_2\text{Et})_2$ under the same conditions gives a green colour and fluorescence, by which one part of $\text{CO}(\text{CO}_2\text{H})_2$ in 5000 may be detected by pptn. as Ba salt and esterification. This reaction is also given by $(\text{CO}\cdot\text{CO}_2\text{Na})_2$ but not by pyruvic, acetoacetic, oxalic, tartaric, or citric esters. E. G. B.

Dissociation of aconitic acid into the labile molecule $\text{CH}\cdot\text{CO}_2\text{H}$ at the mercury-water interface.—See A., 1938, I, 250.

Preparation of trihydroxyglutaric acid from xylose. N. A. SITSCHEV (J. Appl. Chem. Russ., 1938, 11, 68—82).—Xylose is heated for 2 hr. at 60° with HNO_3 (*d* 1.2—1.25), to give trihydroxyglutaric acid in 37% and $\text{H}_2\text{C}_2\text{O}_4$ in 5—7% yield, with xylonic acid and other unidentified products. R. T.

***l*-Threonic acid β -methyl ether and *l*-threonic acid $\alpha\beta$ -dimethyl ether.** K. GÄTZI and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 195—205).—*l*-Arabinose is hydrogenated (Raney Ni) at room temp. and pressure to *l*-arabitol, the CHPh derivative of which is oxidised by $\text{Pb}(\text{OAc})_4$ to benzylidene-*l*-threose, m.p. $119\text{--}120^\circ$ (corr.), hydrolysed by acids to *l*-threose. 1 : 2-*iso*Propylidene-*l*-threose is methylated (Ag_2O and MeI in Et_2O) to 1 : 2-*isopropylidene*-*l*-threose 3-*Me* ether, b.p. $87\text{--}89^\circ/12\text{ mm.}$, hydrolysed by 10% AcOH at 100° to non-cryst. *l*-threose 3-*Me* ether, which is oxidised by $\text{Br}\cdot\text{H}_2\text{O}$ to *l*-threonolactone β -*Me* ether (I) which could not be distilled. *Me* ethylidene-*l*-threonate, m.p. $141\text{--}142^\circ$, Ag_2O , MeI, and Et_2O yield *Me* $\alpha\gamma$ -ethylidene-*l*-threonate β -*Me* ether (II), m.p. $49\text{--}50^\circ$ (corr.), $[\alpha]_D^{25} +46.4^\circ\pm 2^\circ$ in MeOH. This is hydrolysed by 5% NaOH to ethylidene-*l*-threonic acid β -*Me* ether, m.p. $161.5\text{--}162^\circ$ (corr.), $[\alpha]_D^{25} +70.7^\circ\pm 2^\circ$ in H_2O , and transformed by 10% AcOH at 100° into *l*-threonolactone β -*Me* ether, b.p. $83^\circ/0.12\text{ mm.}$, $[\alpha]_D^{25} +19.8^\circ\pm 2^\circ$ in MeOH. Ethylidene-*l*-threonamide has m.p. $155\text{--}156^\circ$, $[\alpha]_D^{25} +103.0^\circ\pm 2^\circ$ in MeOH. $\text{NH}_3\text{-MeOH}$ transforms (II) into ethylidene-*l*-threonamide β -*Me* ether, m.p. $114\text{--}116^\circ$, $[\alpha]_D^{25} +22.8^\circ\pm 2^\circ$ in MeOH. With $\text{NH}_3\text{-MeOH}$ (I) gives *l*-threonamide β -*Me* ether, m.p. about $78\text{--}81^\circ$, $[\alpha]_D^{25} +57.4^\circ\pm 3^\circ$ in MeOH. With a large excess of CH_2N_2 in dioxan (I) affords *l*-threonolactone $\alpha\beta$ -*Me*₂ ether, characterised by conversion into *l*-threonamide $\alpha\beta$ -*Me*₂ ether (III), m.p. $149.5\text{--}150.5^\circ$, $[\alpha]_D^{25} +64.8^\circ\pm 2^\circ$ in MeOH. *l*-Threonolactone α -*Me* ether is transformed by Ag_2O , MeI, and Et_2O into *l*-threonolactone $\alpha\beta$ -*Me*₂ ether, b.p. $97\text{--}98^\circ/12\text{ mm.}$, and *Me* *l*-threonate $\alpha\beta\gamma$ -*Me*₃ ether (corresponding acid, b.p. $147\text{--}149^\circ/11\text{ mm.}$, $[\alpha]_D^{25} +40.2^\circ\pm 2^\circ$ in MeOH). These are identified by conversion into (III) and *l*-threonamide $\alpha\beta\gamma$ -*Me*₃ ether, m.p. 79° , $[\alpha]_D^{25} +63.7^\circ\pm 2^\circ$ in MeOH, respectively. H. W.

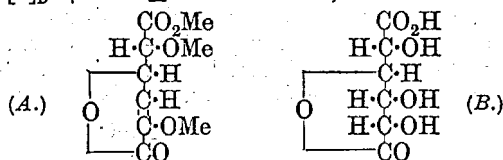
Synthesis of ϵ -deoxy-*l*-ascorbic acid. H. MÜLLER and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 273—277).—Deoxy-*l*-ascorbic acid (I) has marked physiological activity towards guinea-pigs. The presence of one OH in the side-chain appears sufficient for activity but it has not yet been ascertained



whether this must be present in the δ -position. 2 : 3-*iso*Propylidene-*l*-sorbomethyllose is oxidised by KMnO_4 in alkaline solution to α -keto- $\alpha\beta$ -isopropylidene-*l*-gulomethylonic acid [$\alpha\beta$ -isopropylidene-*l*-gulomethyl-*osonic* acid] (II), m.p. $160\text{--}160.5^\circ$ (corr.), $[\alpha]_D^{25} +13.5^\circ\pm 1^\circ$ to $+18.3^\circ\pm 1^\circ$ in H_2O (*Me* ester, m.p. 88°). This is converted by HCl-abs. EtOH into (I), m.p. $167\text{--}168^\circ$ (corr.), $[\alpha]_D^{25} +36.7^\circ\pm 2^\circ$ in 0.01N-HCl (*Pb* salt). H. W.

Constitution of *d*-saccharolactonic acid. O. T. SCHMIDT and P. GÜNTHERT (Ber., 1938, 71, [B], 493—500).—Treatment of *d*-saccharolactonic acid (I)

with MeI and Ag₂O fails to give a uniform product. The use of a large excess of the reactants gives small amounts of the unsaturated lactone-ester (A), m.p. 87°, $[\alpha]_D^{20} + 84.7^\circ \pm 0.5^\circ$ in MeOH, identical with the



substance from (I) and CH₂N₂ and indicating the structure (B) for (I). Pb(OAc)₄ and (I) do not give well-defined products and the resulting solutions are usually devoid of reducing power. (I) is very rapidly attacked by aq. HIO₄ and the dialdehyde ester thus produced is hydrolysed to CHO·CO₂H and (not isolated) *l*-threonic acid, oxidised by Br and CaCO₃ to Ca *d*-tartrate, thus establishing the structure (B) for (I). Degradation of Na *d*-saccharolactonate (II) by HIO₄ follows a precisely similar course. If (I) is regarded as a α -OH-acid the configuration of C₍₂₎ is the same as that of *d*-lactic acid. In confirmation, $[M]_D$ of (II) exceeds that of (I). Further, addition of HCl to a solution of (II) and Na₂MoO₄ causes very marked increase in the dextrorotation, which attains its max. when (II) : HCl = 1 : 1. The optical behaviour therefore confirms the structure (B) for (I).

H. W.

Thio-acids. (MLLE.) F. BLOCH (Compt. rend., 1938, 206, 679—682; cf. A., 1937, II, 418).—Interaction of the Na salts of the appropriate thio-acids (I) with EtI affords Et thio-acetate, -propionate, -butyrate, -isobutyrate, and -benzoate. The theory underlying the existence of isomeric esters of (I) is discussed.

J. L. D.

Oxygen exchange reactions of organic compounds and water.—See A., 1938, I, 257.

Catalytic action of monoses in condensation of formaldehyde to sugars. V. Course of reaction in presence of concentrated salt solutions. A. KUZIN (Biochimia, 1938, 3, 16—27; cf. A., 1937, II, 176).—Sugars are formed from CH₂O in presence of catalysts (fructose, OH·CH₂·CH₂·CHO, ascorbic acid) in saturated Ca(OAc)₂ solution at 100°, but not at 37°; the p_H rises from 7 at 37° to 8.4 at 100°. In supersaturated Mg(OH)·OAc the reaction takes place at 37°; at p_H 8.2.

R. T.

Enzymic oxidation of acetaldehyde in the presence of yeast. K. HEICKEN (Annalen, 1938, 534, 68—94).—Determination of the respiration quotient and periodic analysis of the products of the enzymic oxidation of MeCHO in presence of yeast shows that until the [MeCHO] is very low the amount of EtOH formed corresponds with half the amount of MeCHO which has reacted. MeCHO is therefore first disproportionated to EtOH and AcOH, which is preferentially oxidised to CO₂. Dehydrogenation of EtOH does not occur until MeCHO is practically exhausted; in proportion as this occurs the respiration quotient approaches the val. 0.8. Enzymic oxidation of MeCHO by yeast is therefore the simplest oxidative fermentation. By the aid of O₂ the dismutation products EtOH and AcOH are smoothly converted into H₂O and CO₂ and these products

are not used by the yeast cell for the synthesis of carbohydrates and fats. The reaction is not influenced qualitatively by a phosphate buffer but as p_H diminishes the rate of change of MeCHO increases whereas that of AcOH diminishes. With AcOH + EtOH as substrate dehydrogenation of EtOH takes place much more rapidly than that of AcOH. When EtOH and MeCHO are used, the rates of dehydrogenation of the two substrates are essentially dependent on their concn. and affinity for the enzyme. Increase of [EtOH] causes this compound to be more rapidly dehydrogenated than AcOH in spite of the presence of relatively large amounts of MeCHO. This relationship establishes the identity of the EtOH and AcOH dehydrogenase. The rate of reaction of MeCHO diminishes with increase in [EtOH]. It appears that under these conditions both MeCHO and AcOH are more and more completely displaced from the active enzyme surface. Hence probably MeCHO is not activated by a sp. mutase but by a dehydrogenase identical with that active towards EtOH and AcOH. With MeCHO and AcOH as substrate, the MeCHO undergoes primarily dismutation and dehydrogenation of the products falls first on AcOH. The contradictory observations on the affinity of EtOH and AcOH to the active enzyme surface become explained if it is assumed that MeCHO can function as H acceptor for AcOH or for an intermediate produced by the degradation of AcOH; this ability is present in enhanced measure in nascent MeCHO. The rate at which MeCHO is attacked under N₂ is about 40—50% < that under O₂. With increasing p_H of the reaction liquid the rate increases under either condition. Since even in presence of O₂ the bulk of the MeCHO undergoes dismutation (and is not directly oxidised to AcOH) the difference in the rates cannot be due to a different mechanism of reaction. The greater rate in the presence of O₂ is possibly due to the utilisation for the activation of the dismutation reaction of part of the energy liberated by the oxidation of AcOH.

H. W.

Condensation of chloral with urethanes. Study of the group NH·CH(OH)·CCl₃. A. N. MELDRUM and D. B. PANDYA (J. Univ. Bombay, 1937, 6, Part II, 114—115).—CCl₃·CHO and the appropriate urethane condense to give *chloral-propyl*-, m.p. 75° (*Me ether*, m.p. 57—58°; *anhydro-derivative*, m.p. 94.5°; *Ac derivative*, b.p. 150—153°/17 mm.; *Bz derivative*, m.p. 99—100°), and *isobutyl-urethane*, m.p. 116° (*Me ether*, m.p. 66—67°; *anhydro-derivative*, m.p. 106—107°; *Ac derivative*, m.p. 59—61°; *Bz derivative*, m.p. 122—123°). *Ac*, m.p. 54.5°, and *Bz derivatives*, m.p. 178—179°, of *chloral-methyl*-, and *Ac*, b.p. 155—159°/16 mm., and *Bz derivatives*, m.p. 126—127°, of *chloral-ethyl-urethane* are also described.

F. R. S.

Citral and its sulphonates. F. D. DODGE (Amer. Perf., 1936, 32, No. 3, 67—69).—A general review. Sulphonates (HSO₃ compounds) are classed as *O*-sulphonates (from saturated aldehydes and ketones), α -sulphonates (from $\alpha\beta$ -unsaturated compounds), and ω -sulphonates (formed by addition to other than $\alpha\beta$ -double linkings). The citral disulphonates are regarded as *O* α (labile) and $\omega\omega$ (stable). CH. ABS. (r)

C_{18} hydroxy-aldehyde in the pulp of the olive. H. MARCELET (Compt. rend., 1938, 206, 529—530).—Hot Et_2O or C_2HCl_3 extracts from the pulp, free from fat, *aldoleol* (amorphous), $C_{18}H_{36}O_4$, m.p. 246° (Ac, m.p. 195° , Bz, m.p. 170° , Hg, m.p. 211° and Br-, m.p. 205° derivatives; *phenylhydrazone*, m.p. 241° ; *oxime*, m.p. 200°). J. L. D.

Mechanism of oxidation of organic compounds with selenium dioxide. II. Oxidation of ketones and aldehydes. N. N. MELNIKOV and M. S. ROKITSKAJA (J. Gen. Chem. Russ., 1937, 7, 2738—2747; cf. A., 1938, II, 2).—Oxidation of ketones ($COMe_2$, $COMeEt$, $COMePr$, and *cyclohexanone*) by H_2SeO_3 in H_2O or aq. $AcOH$ proceeds via addition of SeO_2 to the ethylenic linking of the enolic form of the ketone, followed by elimination of H_2O and Se, to yield diketones; the velocity of the reaction is expressed by an equation of the bimol. type. R. T.

Reactions of ketals. A. A. BAUM and G. F. HENNION (J. Amer. Chem. Soc., 1938, 60, 568—571).—Interaction of $CR_2(OR')_2$ with $R''OH$ in presence of a little mineral acid to give $CR_2(OR'')_2$ proceeds by way of the vinyl ether. $CMeBu^a(OMe)_2$ and $BzCl$ react at 100° by way of $MeOH$ and $OMe \cdot CMe^a \cdot CH_2$ to give $MeOBz$ and $OMe \cdot CMe^a \cdot BzCl$; the last-mentioned product is not isolated, but decomposes to $MeCl$ and $COMeBu$; some HCl is also liberated. This mechanism is confirmed by the interaction of $OMe \cdot CMe^a \cdot CH_2$ with HBr to give $MeBr$ and $COMeBu^a$, but with $BzCl$ only polymerisation and evolution of a little HCl occur. With Ac_2O at 150° $CMeBu^a(OMe)_2$ gives $MeOAc$; $C_5H_{11} \cdot CMe(OMe)_2$ (I) gives $MeOAc$ (85%), $AcOH$ (69%), $C_5H_{11} \cdot C(OMe) \cdot CH_2$, and $COMe \cdot C_5H_{11}$. $CMeBu^a(OMe)_2$ with Bu^aOH and a little $p\text{-}C_6H_4Me \cdot SO_3H$ gives Bu^aOMe (44%) and $COMeBu^a$ (85%); (I) similarly gives Bu^aOMe , $COMe \cdot CH_2$ (10% as dibromide), and $COMe \cdot C_5H_9$; $OMe \cdot CMe^a \cdot CH_2$ does not react. The following reactions are postulated: $CMeR(OMe)_2 \rightarrow OMe \cdot CR \cdot CH_2$ (A) + $MeOH$; $Bu^aOH \rightarrow CMe_2 \cdot CH_2 + H_2O$; (A) + $H_2O \rightarrow COMeR + MeOH$; $CMe_2 \cdot CH_2 + MeOH \rightarrow Bu^aOMe$. R. S. C.

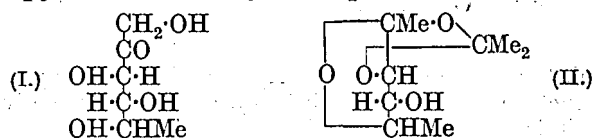
Transformations of hexoses in heavy water.—See A., 1938, I, 261.

Heavy oxygen content of carbohydrates. N. MORITA, K. GOTO, and T. TITANI (Bull. Chem. Soc. Japan, 1938, 13, 99—110).—Isotopic analysis of the H_2O obtained by combustion of sucrose, cotton, and cedar-wood indicates that the excessive contents of ^{18}O and D, as compared with ordinary H_2O , cause increases in the d of $5 \pm 1 \times 10^{-6}$ and 1×10^{-6} , respectively. J. W. S.

Rotatory dispersion of sugars in liquid ammonia and in water.—See A., 1938, I, 232.

Ketomethylpentoses. II. 1-Sorbomethylose. H. MÜLLER and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 263—272).—2:3:4:5-Diisopropylidene-fructose 1-*p*-toluenesulphonate is scarcely affected by NaI in $COMe_2$ at 130° whereas extensive decomp. occurs at a higher temp. 2:3-isoPropylidene-*l*-sorbosose is transformed by $p\text{-}C_6H_4Me \cdot SO_2Cl$ in $C_5H_5N \cdot CHCl_3$ into 2:3-isopropylidene-*l*-sorbose 1:6-di-*p*-toluenesulphonate, m.p. 131° (corr.), $[\alpha]_D^{25} + 8.85^\circ \pm$

0.5° in abs. $EtOH$, converted by NaI in $COMe_2$ at $90\text{--}100^\circ$ into 6-iodo-2:3-isopropylidene-*l*-sorbo-methyl-ose 1-*p*-toluenesulphonate, m.p. $139\text{--}140^\circ$ (corr.), $[\alpha]_D^{25} + 25^\circ \pm 1^\circ$ in abs. $EtOH$. This is transformed (H_2 -Raney Ni) into 2:3-isopropylidene-*l*-sorbo-methyl-ose 1-*p*-toluenesulphonate, m.p. $142\text{--}144^\circ$ (corr.), $[\alpha]_D^{25} + 14.0^\circ \pm 0.5^\circ$ in abs. $EtOH$, hydrolysed to 2:3-isopropylidene-*l*-sorbo-methyl-ose, m.p. 64° , and thence to



1-sorbomethyl-ose [6-deoxy-*l*-sorbose] (I), m.p. 88° , $[\alpha]_D^{25} + 27.7^\circ \pm 0.5^\circ$ in H_2O , which does not react with *o*- or *p*-nitro- or *p*-bromo-phenylhydrazine or with *p*-bromobenzhydrazide; the *phenylosazone* has m.p. $184\text{--}185^\circ$ (corr.). (I) is also obtained by the oxidative fermentation of *l*-galomethylitol by the sorbose bacteria. 2:3-isoPropylidene-*l*-sorbose 1-*p*-toluenesulphonate is converted by NaI in $COMe_2$ at 125° into 1-iodo-2:3-isopropylidene-*l*-deoxy-*l*-sorbo-methyl-ose, m.p. $107\text{--}108^\circ$ (corr.), $[\alpha]_D^{25} - 11.4^\circ \pm 2^\circ$ in abs. $EtOH$, converted (H_2 -Raney Ni) into 2:3-isopropylidene-*l*-deoxy-*l*-sorbo-methyl-ose (II), m.p. $69\text{--}70^\circ$, $[\alpha]_D^{25} + 20.0^\circ \pm 0.7^\circ$ in abs. $EtOH$. H. W.

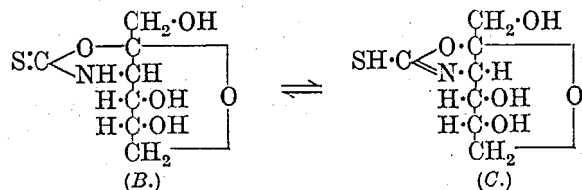
Action of phosphate on hexoses. III. Simultaneous formation of acetol and pyruvic acid from glucose. R. NODZU, K. MATSUI, R. GOTO, and S. KUNICHIKA (Mem. Coll. Sci. Kyoto, 1937, 20, A, 197—206; cf. A., 1936, 55).—When distilled with Na or K phosphate at p_H 4—7, glucose gives small amounts of acetol and $AcCO_2H$, even in absence of air; a little $OH \cdot CHMe \cdot CO_2H$ is also formed, particularly at p_H 8.4. *dl*-Glyceraldehyde and $AcCHO$ afford mere traces of acetol and $AcCO_2H$ under similar conditions, and these products probably arise by direct disproportionation and fission of glucose. The poor yields are ascribed to instability of the products under the reaction conditions. R. S. C.

Reaction for distinguishing fructose from glucose. E. V. ZMACZYNSKI (J. Gen. Chem. Russ., 1937, 7, 2861—2862).—A mixture of the sugar with S is heated with glycerol containing $Pb(OAc)_2$; a black coloration appears in presence of fructose, but not of glucose, sucrose, maltose, or lactose. The mechanism of the reaction is discussed. R. T.

Behaviour of fructose towards thiocyanic acids. G. ZEMPLÉN, A. GERECOS, and E. ILLÉS (Ber., 1938, 71, [B], 590—596).—Addition of HCl (d 1.19) to fructose (I) and $KCNS$ at 0° gives fructose-thiocyanic acid I [(A); $R = N:C:S$ or $S:C:N$], m.p. 218° , $[\alpha]_D^{25}$

-44.49° in H_2O , which does not afford NH_3 when heated with $NaOH$. S cannot be smoothly removed from it by H_2O_2 but is quantitatively oxidised to H_2SO_4 by I and alkali; since 6 I are thereby used the presence of unchanged CNS is established. In much more conc. solution (I), $KCNS$, and HCl yield fructose-thiocyanic acid II [μ -thiofructoxazoline] (II) (B or C), m.p. 183.5° (decomp.), $[\alpha]_D^{25} - 50.92^\circ$ in H_2O . Neither (A) nor (II) reduces

Fehling's solution directly or after hydrolysis; $[\alpha]_D$ of both changes stoichiometrically with addition of 0.1N-

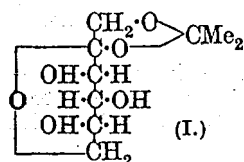


NaOH. In alkaline solution S can be oxidised quantitatively to H_2SO_4 by H_2O_2 or Br, best by OI^- whereby 8 I are required; the S-free compound could not be obtained cryst. $\text{NHPh} \cdot \text{NH}_2 \cdot \text{HCl}$ and NaOAc transform (II) into phenylglucosazone. A cryst. Ac derivative could not be obtained. BzCl , (II), and $2\text{N} \cdot \text{NaOH}$ give μ -thiolfructoxazoline tribenzoate, m.p. 173° , $[\alpha]_D^{20} -46.48^\circ$ in CHCl_3 . CPh_3Cl and (II) in abs. $\text{C}_5\text{H}_5\text{N}$ give μ -thiolfructoxazoline CPh_3 ether, m.p. 77° (decomp.) after softening at 55° . H. W.

Calcium chloride compound of α -l-sorbose. R. L. WHISTLER and R. M. HIXON (J. Amer. Chem. Soc., 1938, 60, 729).—Sorbose gives the compound, sorbose, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, m.p. 159° (corr.), $[\alpha]_D^{20} -24.2^\circ \rightarrow -23.9^\circ$ in H_2O (cf. sorbose), acetylation of which gives the keto-penta-acetate. R. S. C.

α -Ethyl-l-sorbosepyranoside and its tetra-acetate. R. L. WHISTLER and R. M. HIXON (J. Amer. Chem. Soc., 1938, 60, 563—564).—l-Sorbose and dry $\text{HCl} \cdot \text{EtOH}$ give α -ethyl-l-sorbosepyranoside, m.p. $115-116^\circ$, $[\alpha]_D^{15} -73.9^\circ$ in H_2O (const.), converted by $\text{Ac}_2\text{O} \cdot \text{C}_5\text{H}_5\text{N}$ into the 1:3:4:5-tetra-acetate, m.p. $74-75^\circ$, $[\alpha]_D^{15} -54.6^\circ$ in CHCl_3 , obtained also from sorbose tetra-acetate and $\text{Ag}_2\text{O} \cdot \text{EtI}$ (proving its structure). The rates of formation and hydrolysis of the Et sorboside are similar to those of the Me analogue. R. S. C.

isoPropylidene compounds of sugars and their derivatives. XX. New isopropylidene-l-sorbose. H. OHLE (Ber., 1938, 71, [B], 562—568). Sorbose is converted by COMe_2 and conc. H_2SO_4 mainly into diisopropylidenesorbose accompanied by about 3% of isopropylidene- α -l-sorbosepyranose (I), m.p. $142-143^\circ$, $[\alpha]_D^{20} -85.2^\circ$ in H_2O . In presence of anhyd. CuSO_4 the sugar is unaffected by pure COMe_2 , but with COMe_2 of b.p. $56-58^\circ$ the yield of (I) exceeds



that obtained by use of H_2SO_4 ; an unidentified strongly reducing substance is also produced in considerable amount. (I) is readily hydrolysed by $\text{N} \cdot \text{H}_2\text{SO}_4$ at 36° , is unchanged by further treatment with CuSO_4 and COMe_2 , and gives a well cryst. triacetate, m.p. $88-89^\circ$, $[\alpha]_D^{20} -72.8^\circ$ in CHCl_3 , through which it is best isolated, but a non-cryst. benzoate. With $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{SO}_2\text{Cl}$ in anhyd. $\text{C}_5\text{H}_5\text{N}$ at 20° (I) very slowly yields 1:2-isopropylidene- α -l-sorbosepyranose di-*p*-toluenesulphonate, m.p. $127.5-128.5^\circ$, $[\alpha]_D^{20} -77.8^\circ$ in CHCl_3 ; 2:3-isopropylidene-l-sorbofuranose di-*p*-toluenesulphonate has m.p. $128.5-129.5^\circ$, $[\alpha]_D^{20} +141^\circ$ in CHCl_3 . With CPh_3Cl (I) does not react whereas 2:3-isopropylidene-l-sorbofuranose and CPh_3Cl in CHCl_3 slowly yield a non-cryst. material

which gives 1:6-ditriphenylmethyl-2:3-isopropylidene-l-sorbofuranose 4-acetate, m.p. $224-225^\circ$, $[\alpha]_D^{20} +23.0^\circ$ in CHCl_3 . Reasons are advanced for considering the free sugar to be α -l-sorbosepyranose.

H. W.

Glucoside from bark of *Rhamnus japonica*. Z. NIKUNI (J. Agric. Chem. Soc. Japan, 1938, 14, 352—361).—Prep. and properties of α -sorinin, $\text{C}_{24}\text{H}_{28}\text{O}_{14}$, m.p. 159° , are described. Hydrolysis with H_2O at 100° for 30 min. yields α -sorigenin, $\text{C}_{13}\text{H}_{10}\text{O}_5$, m.p. $227-229^\circ$ (diacetate; Me_1 and Me_2 ethers), and primverose. J. N. A.

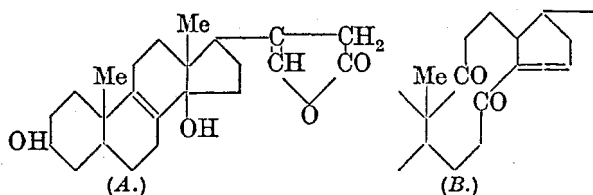
N-Glucosides and the Amadori isomerisation.

R. KUHN and L. BIRKOFER (Ber., 1937, 71, [B], 621—633).—The formation of N-glucosides from amines and hexoses or pentoses is effected (a) in EtOH without catalyst in which cases the presence of NH_4Cl impedes the crystallisation of the product, (b) in presence of NH_4Cl , without which the change does not occur or takes place very slowly, (c) by use of HCl in preference to NH_4Cl . In EtOH , NH_4Cl can be titrated as free HCl . During the condensation of amines with sugars in presence of NH_4Cl , NH_3 is liberated. It is uncertain whether the isoglucosamines, obtained by the Amadori isomerisation of the N-glucosides, contain a five- or six-membered ring. The cryst. members appear to be β forms since they show upward mutarotation. The postulated intermediate formation of Schiff's bases during the transformation requires that it should not occur with the glucosides of sec. bases. This appears to be the case but the change is frequently not observed with glucosides of primary bases and, so far, is restricted to derivatives of glucose. The certain formation of a Schiff's base from a primary amine and a reducing sugar has not yet been established. The following compounds have been obtained by the method indicated by the letter in parenthesis: p-phenetidine-d-fructoside (b), m.p. 14° (decomp.), $[\alpha]_D^{21} -187^\circ$ in $\text{C}_5\text{H}_5\text{N}$, from d-fructose; p-phenetidine-l-sorboside (b), m.p. 160° (decomp.), $[\alpha]_D^{22} -191^\circ$ in $\text{C}_5\text{H}_5\text{N}$; p-phenetidine-d-galactoside (b), m.p. 155° (decomp.), $[\alpha]_D^{20} -102^\circ$ in $\text{C}_5\text{H}_5\text{N}$, also obtained by fusing the reactants together; p-phenetidine-d-mannoside (b), m.p. 157° (decomp.), $[\alpha]_D^{15} -155^\circ$ to -145° in $\text{C}_5\text{H}_5\text{N}$ in 24 hr., hydrogenated (Ni, $75^\circ/45$ atm.) to N-p-phenetidine-d-mannosamine (I), m.p. 188° , $[\alpha]_D^{21} +22^\circ$ in $\text{C}_5\text{H}_5\text{N}$; N-p-phenetidine-d-isoglucosamine, from d-glucose and p- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$ at 80° or in boiling 96% EtOH , hydrogenated to (I); p-phenetidine-lactoside (b), (+1 H_2O); m.p. 139° (decomp.), $[\alpha]_D^{21} -26^\circ$ in $\text{C}_5\text{H}_5\text{N}$; 3:4-dimethylaniline-d-glucoside (b), (+1 H_2O), $\text{C}_5\text{H}_5\text{N}$ (indef.) $84-102^\circ$, $[\alpha]_D^{21} -107^\circ$ in $\text{C}_5\text{H}_5\text{N}$, reduced (Cr-Ni) to N-3:4-dimethylphenyl-d-glucosamine, m.p. 131° , $[\alpha]_D^{22} -19^\circ$ in $\text{C}_5\text{H}_5\text{N}$; 3:4-dimethylaniline-d-mannoside (b), m.p. $184-185^\circ$, $[\alpha]_D^{22} -174^\circ$ in $\text{C}_5\text{H}_5\text{N}$, reduced (Ni) to N-3:4-dimethylphenyl-d-mannosamine (II), m.p. 182° , $[\alpha]_D^{22} +14^\circ$ in $\text{C}_5\text{H}_5\text{N}$; N-3:4-dimethylphenyl-d-isoglucosamine, m.p. 162° , $[\alpha]_D^{20} -61^\circ$ to -26° (equilibrium) in $\text{C}_5\text{H}_5\text{N}$, hydrogenated (PtO₂ in abs. EtOH) to (II); 3:4-dimethylaniline-l-arabinoside (a), m.p. 139° (decomp.), $[\alpha]_D^{21} -90^\circ$ in $\text{C}_5\text{H}_5\text{N}$, hydrogenated to N-3:4-dimethylphenyl-l-arabamine, m.p. 139° , $[\alpha]_D^{22} -12^\circ$ in $\text{C}_5\text{H}_5\text{N}$; 3:4-dimethylaniline-

d-ribose (a), m.p. 118°, $[\alpha]_D^{25} +172^\circ$ in C_5H_5N (no mutarotation), whence *N*-3:4-dimethylphenyl-*d*-ribamine, m.p. 146°, $[\alpha]_D^{25} -31^\circ$ in C_5H_5N ; *sulphanilamide-d-glucoside* (c), m.p. 195°, or, after long preservation, m.p. 204°, $[\alpha]_D^{25} -123^\circ$ in H_2O without mutarotation, $[\alpha]_D^{25} -125^\circ$ in 0.1N- Na_2CO_3 without hydrolysis, and its *tetra-acetate*, m.p. 189°, $[\alpha]_D^{25} -86^\circ$ in C_5H_5N ; *sulphanilamide-d-mannoside* (b), m.p. 202°, $[\alpha]_D^{25} -163^\circ$ in C_5H_5N without mutarotation; *sulphanilamide-l-arabinoside* (b), m.p. 194°; *piperidine-d-glucoside* (a), m.p. 115°, $[\alpha]_D^{25} -43^\circ$ to -13° (final val.) in C_5H_5N , and its *tetra-acetate*, m.p. 122°; *dibenzylamine-d-glucoside* (b), m.p. 159—160° (darkening), $[\alpha]_D^{25} -88^\circ$ to -40° (final val.) in C_5H_5N ; *o-aminophenol-N-d-glucoside* (c), m.p. 148—150°, $[\alpha]_D^{25} -88^\circ$ to $+12^\circ$ (final val.) in H_2O , methylated (CH_2N_2) and then hydrolysed to *o*- $NH_2 \cdot C_6H_4 \cdot OMe$.

H. W.

Vegetable heart poisons. XVI. Constitution of adynerin. R. TSCHESCHE and K. BOHLE (Ber., 1938, 71, [B], 654—660; cf. Neumann, A., 1937, II, 369).—Adynerin (I) is $C_{30}H_{44}O_7$, and is probably an oleandroseglucoside. Adynerigenin (II), $C_{23}H_{32}O_4$, contains two double linkings of which only one can be hydrogenated catalytically. Two of the four O are present in a lactone group, the others in OH groups of which one is *sec.* and can be acetylated by Ac_2O whereas the other is *tert.* and probably attached to C_{14} . It is involved in the production of *isoadynerin*, $C_{30}H_{44}O_7 \cdot 2H_2O$, m.p. 150—152° (decomp.), $[\alpha]_D +4.9^\circ$ in $CHCl_3$. Dil. acids readily transform (II) into *anhydroadynerigenin* (III), $C_{23}H_{30}O_3$, m.p. 176—178°, $[\alpha]_D -109^\circ$ in $CHCl_3$ (*acetate*, m.p. 152—154°, $[\alpha]_D -105.5^\circ$ in $CHCl_3$), the absorption spectrum of which establishes the presence of conjugated double linkings in vicinal rings; the new double linking is probably



at C_{18-9} . Treatment of (III) with dil. acid leads to an isomeric *product*, m.p. 235°, $[\alpha]_D +147^\circ$ in $CHCl_3$, which contains the conjugated linkings in the same ring. It absorbs 3 H_2 , giving a non-cryst. product, whereas (III) affords *tetrahydroanhydroadynerigenin* (IV), m.p. 170—172°, $[\alpha]_D +32^\circ$ in $CHCl_3$. On the likely assumption that (I) has the cholane ring system, it has probably the structure (A). Oxidation of (III) by CrO_3 in $AcOH$ gives a *ketone*, $C_{22}H_{28}O_5$, m.p. 270—272°, shown by its absorption spectrum to be $\alpha\beta$ -unsaturated and probably represented by (B). Under similar conditions (IV) gives a neutral substance, $C_{23}H_{32}O_5$, m.p. 265—268°, which does not show absorption in the ultra-violet and contains 1 active H.

H. W.

Glucosides of the sterol and sex hormone series. Stereochemistry of epimeric alcohols. K. MIESCHER and W. H. FISCHER [with L. EHMANN] (Helv. Chim. Acta, 1938, 21, 336—356).—Treatment of dehydroandrosterone with acetobromoglucose (I)

and Ag_2O in Et_2O slowly affords β -*tetra-acetylglucosidodehydroandrosterone* (II), m.p. 192—193.5°, in 40—50% yield. β -*Glucosidodehydroandrosterone*, m.p. 223—225°, is very sparingly sol. in H_2O . 3-Dehydroandrosterone acetate is transformed by 30% H_2O_2 in $AcOH$ followed by $KOH-MeOH$ into 3:5:6-*trihydroxyandrostan-17-one* (III), m.p. 298—300° (decomp.), and by BzO_2H in $CHCl_3$ at -10° into 3-*hydroxy-5:6-oxidoandrostan-17-one* (IV), m.p. 229—230°, converted by H_2O at 100—110° into (III). (III) and (IV) are very sparingly sol. in Et_2O and, when treated with (I) and Ag_2O in boiling C_6H_6 , yield only very small amounts of glucoside; the action of H_2O_2 on (II), however, affords 3- β -*tetra-acetylglucosido-5:6-dihydroxyandrostan-17-one*, hydrolysed to 3- β -*glucosido-5:6-dihydroxyandrostan-17-one* ($+2H_2O$), m.p. 275° (decomp.) after softening at 180°, which is freely sol. in warm, sparingly in cold H_2O . *iso*Androsterone readily gives the corresponding *glucoside* ($+H_2O$), m.p. 216—217°, whereas androsterone fails to react. Similarly *epicholesterol* does not react with (I) in Et_2O at room temp. or in boiling C_6H_6 , whereas *cholesterol* readily gives 3- β -*tetra-acetylglucosidocholesterol*, m.p. 174—175°. In the *allocholane* series the power to react with glucose is parallel to the ability to add digitonin. 3- β -*Tetra-acetylglucosidocoprosterol*, m.p. 198—200°, is readily prepared whereas *epicoprosterol* does not react. *iso*Borneol does not react with (I). The contrasting behaviour of the epimeric alcohols thus observed leads to a general account of the stereochemistry of these and similar substances. Consideration is given to those with one additional substituent in the ring (*cyclohexane* type), with two additional substituents (*decahydronaphthalene* type), and with three additional substituents (*cholesterol* and *allocholesterol* types; saturated sterol type; sex hormones; terpenes).

H. W.

Choline-d-glucoside tetra-acetate. E. L. JACKSON (J. Amer. Chem. Soc., 1938, 60, 722—723).—Acetoglucosidyl bromide (0.22 mol.), $CH_2Cl \cdot CH_2 \cdot OH$ (3.33 mols.), and Ag_2CO_3 in C_6H_6 give 69% of β -*chloroethyl- β -d-glucoside tetra-acetate*, m.p. 118.5—119.5° (corr.), $[\alpha]_D^{25} -13.7^\circ$ in $CHCl_3$, converted slowly by $NMe_3 \cdot HCl$ in C_6H_6 , first at 62—64° and then at 50—52°, into *trimethyl- β -d-glucosidoethylammonium chloride* (85%), m.p. 230°, $[\alpha]_D^{25} -25.6^\circ$ in H_2O , -13.5° in $CHCl_3$, which with $NaOH$ gives a laevorotatory solution. $[\alpha]_D$ for the Ac-free salt is calc. to be about -27° in H_2O ; thus the product of Schroeter *et al.* (A., 1931, 778) was the α -glucoside.

R. S. C.

So-called limit decomposition of starch. K. MYRBÄCK, B. ÖRTENBLAD, and K. AHLBORG (Compt. rend. Trav. Lab. Carlsberg, 1938, 22, 357—365; cf. A., 1937, III, 431).—When amylase acts on starch, maltose and substances of higher mol. wt. are produced. These are not attacked by amylase and are called limit dextrins. They are not secondary products, but are non-hydrolysable parts of the starch mol. Probably none has been obtained pure, and the prep. of nine fractions from potato starch by action of taka-diastase is described. These differ in mol. wt., % of P, and amount of glucose formed on reduction. Their constitution is unknown, and the fractions with low mol. wt. give bromoacetyl derivatives which

yield only traces of maltose hepta-acetate on hydrolysis, so that the dextrans cannot be composed of maltose units.

J. N. A.

Starch. K. FREUDENBURG, H. BOPPEL, and M. MEYER-DELIUS (Naturwiss., 1938, 26, 123).—Methylation of unbleached native starch (I) with Na and MeI in liquid NH_3 at -40° gave a Me derivative (OMe 44.5%) from which on hydrolysis tetra- (1%) and di-methylglucose (6%) were isolated; hence (I) is a chain of 80–100 units. Schardinger's α -dextrin (II) formed a Me derivative (OMe 45.5%) which yielded only 2 : 3 : 6-trimethylglucose on hydrolysis. (II) may be a ring of 5 maltose units and may not be pre-formed in (I), which is possibly constituted of loops or knots. Complete methylation of (I) decreases its viscosity by breaking these loops.

M. S.

End-group in cellulose. K. FREUDENBURG and E. PLANKENHORN (Naturwiss., 1938, 26, 124).—Cold methylation of unbleached ramie (I) with Me_2SO_4 gave a Me derivative (OMe 44.0%) which yielded 0.05% of tetramethylglucose (II) on hydrolysis. Methylation of (I) with Na and MeI in liquid NH_3 at -40° gave a Me derivative (OMe 45.0%) which yielded 0.2% of (II) on hydrolysis; hence the degree of polymerisation of (I) was depressed from 2000 to 500. (I) may consist of looped macromols. in aggregation which disperse to single macromols. only under special conditions.

M. S.

Wood cellulose. V. "Trimethylated" cellulose from *Thiriena* pulp. D. J. BELL (Biochem. J., 1938, 32, 699–701).—Wood cellulose has been methylated to a OMe content >43%. The product, $[\alpha]_D^{20}$ in CHCl_3 , is converted to the extent of >90% by HCl-MeOH at 80° into simple glucosides among which 2 : 3 : 6-trimethylglucose is identified.

P. G. M.

Aliphatic polyamines. VII. J. VAN ALPHEN (Rec. trav. chim., 1938, 57, 265–276).— $\text{C}(\text{CH}_2\text{Br})_4$ with EtOH-NH_3 + conc. aq. NH_3 at $160^\circ/8$ hr. yields, with difficulty, highly condensed amines and a little *tetrakis*(aminomethyl)methane, $+\text{H}_2\text{O}$, b.p. $278-282^\circ$ [tetrapicrate, decomp. $206-208^\circ$; *tetra*-(phenylthiocarbamyl) derivative, decomp. 150°]; the presence of the 4 NH_2 is shown by reducing the condensation product with PhCHO , with Na and EtOH , to *tetrakis*(benzylaminomethyl)methane (*tetrahydrochloride*, m.p. $217-218^\circ$). NH_2Me reacts more readily to give *tetrakis*(methylaminoethyl)methane, $+\text{0.5H}_2\text{O}$ (I), b.p. $235-238^\circ$ [tetrapicrate, m.p. $190-195^\circ$; *tetra*-(phenylthiocarbamyl) derivative, m.p. 152°], which with ArCHO forms 3 : 9-diaryl-2 : 4 : 8 : 10-tetramethyl-2 : 4 : 8 : 10-tetra-aza-6-spiroundecane derivatives, $\text{CHAr} \begin{smallmatrix} \text{NMe-CH}_2 \\ \text{NMe-CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}_2\text{-NMe} \\ \text{CH}_2\text{-NMe} \end{smallmatrix} \text{CHAr}$, of which the following are described: 3 : 9-diphenyl-, m.p. 110° ; -di-p-nitrophenyl-, m.p. 230° ; -di-p-chlorophenyl-, m.p. 220° ; -di-p-anisyl-, m.p. 164° ; di-3 : 4-methylenedioxyphenyl-, m.p. 153° . (I) and $\text{CS}_2\text{-EtOH}$ give 2 : 4 : 8 : 10-tetramethyl-3 : 9-dithio-2 : 4 : 8 : 10-tetra-aza-6-spiroundecane, decomp. 260° . (I) and 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2)_2$ in EtOH-NaOAc give a product, m.p. $217-219^\circ$, converted by abs. HNO_3

at -10° into *tetrakis*-(2 : 4 : 6-trinitrophenylnitroaminomethyl)methane, m.p. 117° , decomp. 140° .

$(\text{CH}_2\text{-NH}_2)_2\text{H}_2\text{O}$ and $\text{C}(\text{CH}_2\text{Br})_4$ give *tetrakis*-(β -aminoethylaminomethyl)methane ($+\text{2H}_2\text{O}$) (II), b.p. $265-275^\circ/18$ mm.; [octapicrate, m.p. $120-160^\circ$; *octa*-(phenylthiocarbamyl) derivative, m.p. $130-135^\circ$], which with $\text{CS}_2\text{-EtOH}$ affords *tetrakis*-(2-thiotetrahydro-1-glyoxalinylmethyl)methane, decomp. $>320^\circ$. Reduction of the PhCHO condensation product of (II) gives *tetrakis*-(β -benzylaminoethylaminomethyl)methane, decomp. $140-160^\circ$.

Piperidine and $\text{C}(\text{CH}_2\text{Br})_4$ yield *tetrakis*(piperidino-methyl)methane, m.p. 163° (*tetrahydrochloride*, decomp. $260-300^\circ$). Piperazine hexahydrate similarly yields *tetrakis*-(1-piperazylmethyl)methane, isolated only as the *tetraphenylthiocarbamyl* derivative, m.p. $150-180^\circ$. $\text{N}_2\text{H}_4\text{H}_2\text{O}$ gives a tetrahydrazine derivative [*pentahydrobromide* ($+\text{3H}_2\text{O}$), decomp. 207°], which affords *CHPh*., m.p. $270-330^\circ$, *p-chloro*., m.p. 272° , *p-nitro*., m.p. 178° , and 3 : 4-methylenedioxybenzylidene, m.p. 310° , derivatives. 1 : 4-Di(phenylthiocarbamyl)piperazine sublimes at 285° . A. T. P.

Relative reactivity of amines in the aminolysis of amides. (Miss) M. E. SMITH and H. ADKINS (J. Amer. Chem. Soc., 1938, 60, 657–663).—The equilibrium, $\text{NHR}^1\text{Ac} + \text{NH}_2\text{R}' \rightleftharpoons \text{NHR}'\text{Ac} + \text{NH}_2\text{R}$, in dodecylpiperidine at 260° under H_2 (100 atm.) is investigated, R being *n*-amyl or $\text{CH}_2\text{Ph-CH}_2$, and R' being CHEtBu^a , $[\text{CH}_2]_2$, iso-amyl, CHEt_2CH_2 , CH_2Bu^v , CH_2Ph , cyclohexyl, $\text{CH}_2\text{Pr}^b\text{-CHMe}$, CHMeBu , *n*- $\text{C}_6\text{H}_{13}\text{CHMe}$, or Ph; piperidine is also investigated. Reactivity of an amine is depressed by α -, increased by γ -, and scarcely affected by β -substituents. Ph has a depressant action, the more so the closer it is to the N. The effect is probably steric and is not correlated with the strength of the base. *Acet- α -dimethylbutyl*-, b.p. $94.5-95^\circ/1$ mm., -*n*-amyl-, b.p. $106.5-107.5^\circ/1$ mm., - β -ethylbutyl-, b.p. $107-108^\circ/1.5$ mm., - β -octyl-, b.p. $129-129.2^\circ/1.5$ mm., and - γ -ethylheptyl-amide, b.p. $132.5-133^\circ/1$ mm., γ -ethylheptyl-, b.p. $73-73.5^\circ/11$ mm., and β -ethylbutyl-amine, b.p. $121-122^\circ/725$ mm., are described. R. S. C.

Organic salts of glycine, the alanines, and dl-leucine. M. E. FITZGERALD (Trans. Roy. Soc. Canada, 1937, [iii], 31, III, 153–157).—The following salts have been prepared and their solubilities in H_2O , COME_2 , Et_2O , MeOH , EtOH , and Bu^nOH at room temp. have been determined: glycine (I) trichloroacetate, m.p. 133° (decomp.), benzenesulphonate, m.p. 159.5° , 2 : 5-dichloro-, m.p. 191° , and -dibromo-benzenesulphonate, m.p. 203° , 2-chlorotoluene-5-sulphonate, m.p. 165° , naphthalene-2-sulphonate, m.p. 197° ; α -alanine (II) trichloroacetate, m.p. 134° (decomp.), benzenesulphonate, m.p. 160° , 2 : 5-dichloro-, m.p. 201° , and -dibromo-benzenesulphonate, m.p. 208° , 2-chlorotoluene-5-sulphonate, m.p. 165° , naphthalene-2-sulphonate, m.p. 221° ; β -alanine trichloroacetate, m.p. 136° (decomp.), benzenesulphonate, m.p. 118° , 2 : 5-dichloro-, m.p. 106° and -dibromo-benzenesulphonate, m.p. 210° , 2-chlorotoluene-5-sulphonate, m.p. 124° , naphthalene-2-sulphonate, m.p. 181° ; dl-leucine (III) trichloroacetate, m.p. 136° (decomp.), benzenesulphonate, m.p. 148° , 2 : 5-dichloro-, m.p. 216° ,

and *-dibromo-benzenesulphonate*, m.p. 212°, *2-chloro-toluene-5-sulphonate*, m.p. 165°, *naphthalene-2-sulphonate*, m.p. 203°. All the trichloroacetates are partly decomposed by COMe_2 , CHCl_3 , and C_6H_6 . The acetates of (I), (II), and (III), and the phenylbenzoates, benzoates, *o*-chloro- and *o*-nitro-benzoates, and 2 : 4 : 6-trichlorobenzoates of the four NH_2 -acids do not exist. J. N. A.

Artificial lipoproteins. S. J. VON PRZYŁĘCKI and E. HOFER (*Acta Biol. Exp.*, 1937, 11, 193—196).—Choline (I) yields compounds (not described) with glycine, alanine, leucine, tyrosine, oxypoline, and asparagine at p_{H} 8, but not at p_{H} 3 or 6, whilst with glycerophosphoric acid (II) compounds are formed at p_{H} 3, but not at p_{H} 6 or 8. Aspartic and glutamic acid combine with (I) at p_{H} 3, 6, and 8, and with (II) only at p_{H} 3. Histidine (III), lysine, arginine (IV), guanidine (V), creatine, and clupein (VI) do not combine with (I) at p_{H} 3—8, but combine with diglycylglycine (VII) and peptone (VIII) at p_{H} 6 and 8, but not 3. (II) combines with lysine and (VI) at p_{H} 3—8, with (III), (VII), and creatine at p_{H} 3 and 6, but not 8, and with (IV) and (V) at p_{H} 3 and 8, but not 6; no combination is observed with (VIII). Lecithin yields compounds with (III), (IV), (V), (VI), and (VIII), but not with the remaining NH_2 -acids. It is concluded that $\cdot\text{C}\cdot\text{O}\cdot\text{NH}\cdot$, $\text{OH}\cdot$, $\cdot\text{C}\cdot\text{S}\cdot\text{S}\cdot\text{C}\cdot$, and $\cdot\text{CO}\cdot\text{NH}_2$ groups have no affinity for lecithin, the H_3PO_4 groups of which combine with basic, and the choline- NH_2 groups of which combine with acidic, NH_2 -acids. R. T.

Biochemistry by analogy: sulphur of cystine. B. H. NICOLET (*J. Washington Acad. Sci.*, 1938, 28, 84—93).—An address. J. N. A.

New application of Bredt's rule. R. LUKEŠ (*Coll. Czech. Chem. Comm.*, 1938, 10, 148—152; cf. A., 1924, i, 643).—Theoretical considerations underlying the formation and structure of amides, $\text{R}\cdot\text{C}\cdot\text{O}\cdot\text{NH}_2$, including cyclic types. A. T. P.

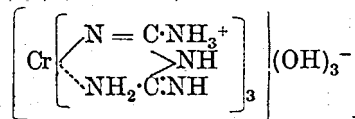
Amides and phenylhydrazides of two epimeric (α - and β -)-*d*-gluco-octonic acids. R. C. HOCKETT and C. S. HUDSON (*J. Amer. Chem. Soc.*, 1938, 60, 622—623).—By the cyanohydrin synthesis *d*- α -gluco-heptose yields *d*- α *, new m.p. 151—152°, $[\alpha]_{\text{D}}^{20} + 53.7^\circ$ in H_2O (*phenylhydrazide*, m.p. 190.5—194°, $[\alpha]_{\text{D}}^{20} - 17.8^\circ$ in H_2O ; *amide*, m.p. 160.5—161.5°, $[\alpha]_{\text{D}}^{20} - 24.4^\circ$ in H_2O), and *d*- β -gluco-octonolactone, m.p. 185.5—186°, $[\alpha]_{\text{D}}^{20} + 24.6^\circ$ in H_2O (*phenylhydrazide*, m.p. 162.5—164.5°, $[\alpha]_{\text{D}}^{20} + 25.9^\circ$ in H_2O ; *amide*, m.p. 125.5—126.5°, $[\alpha]_{\text{D}}^{20} + 12.1^\circ$ in H_2O). $[\alpha]$ are in accordance with known rules and confirm the structures assigned. M.p. are corr. R. S. C.

Oxides of thiocarbamide. III. J. BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1938, 41, 70—75; cf. A., 1936, 1097; 1937, II, 10).—The conductivity of a solution of thiocarbamide dioxide (I) in aq. NH_3 is \gg the val. attributable to either component, and indicates that (I) is acidic in character. Decomp. of (I) occurs more readily in alkaline solution; in presence of KOH , K_2SO_2 is first formed, this being accompanied by a decrease in alkalinity of the solution and an increased tendency to reduce I_2 ,

whilst CdS is pptd. from ammoniacal Cd solutions instead of Cd . No Cd is deposited when alkaline Cd is added to Et_2SO_2 while the latter is undergoing hydrolysis with KOH , or to rongalite, indicating that reduction to Cd by (I) is not attributable to the K_2SO_2 formed. (I) is stable in pure AcOH and in conc. H_2SO_4 . In acid solution it is not oxidised by I_2 , only slowly oxidised by FeCl_3 , and does not absorb atm. O_2 . In aq. NH_3 it absorbs O_2 very rapidly and can be used for the detection of O_2 in gas mixtures. Thiocarbamide trioxide is sol. in H_2O , but the solution is unstable, especially in the presence of NH_3 . In the pure state it is almost neutral. The solid suffers slow decomp. into $\text{CN}\cdot\text{NH}_2$, SO_2 , and H_2O . J. W. S.

Organic reactions with boron fluoride. XX. Acidolysis of esters. F. J. SOWA (*J. Amer. Chem. Soc.*, 1938, 60, 654—656; cf. A., 1938, II, 130).—In presence of $\text{BF}_3\cdot 2\text{AcOH}$ at 100° Pr^a , Bu^a , and Bu^b propionate, benzoate, and salicylate react with AcOH to give the corresponding alkyl acetate with smaller yields of Pr^b , CHMeEt , and Bu^c acetate, respectively. Reaction is thus mainly by way of $\text{CO}_2\text{Et}\cdot\text{CMe}(\text{OH})\cdot\text{OAlk}$ etc. and only slightly by way of the olefine. Et_2SO_4 (0.5 mol.) and AcOH (1 mol.) alone at 100° give up to 44% of EtOAc . For formation of EtOAc from HCO_2Et there is an optimum amount of BF_3 . With H_2SO_4 , ZnCl_2 , BF_3 , and $\text{BHF}_2(\text{OH})_2$ the yields of Bu^aOAc are 21, 31, 40, and 60%, respectively. R. S. C.

Complex compounds of diguanide with trivalent metals. I. Chromium diguanides. P. RÂX and H. SAHA (*J. Indian Chem. Soc.*, 1937, 14, 670—684).— $\text{K}_2\text{SO}_4\cdot\text{Cr}_2(\text{SO}_4)_3$ and diguanide sulphate in aq. NaOH give chromium trisdiguanide monohydrate (I), $[\text{Cr}(\text{R}_3)_3]\cdot\text{H}_2\text{O}$ ($\text{R} = \text{C}_2\text{H}_4\text{N}_2$) (Δ , mol. wt. from f.p., and χ determined), which in H_2O behaves as the tri-acid base $[\text{Cr}(\text{RH})_3](\text{OH})_3$ (II) [*hydrochloride*, $[\text{Cr}(\text{RH})_3]\text{Cl}_3$ (Δ decreases on keeping); *hydrobromide*; *hydroiodide*; *sulphate*, $[\text{Cr}(\text{RH})_3](\text{SO}_4)_3\cdot 2\text{H}_2\text{O}$; *nitrate*; *nitrite*; *chloroformate*; *carbonate*; *hydrosulphide*; *chlorosulphite*, $[\text{Cr}(\text{RH})_3](\text{SO}_3\text{Cl})\cdot\text{H}_2\text{O}$; *hydroxosulphite*, $[\text{Cr}(\text{RH})_3](\text{OH})(\text{SO}_3)\cdot 2.5\text{H}_2\text{O}$; *chlorothiosulphate*; *thiosulphate*; *chlorochromate*, $[\text{Cr}(\text{RH})_3]\text{CrO}_4\text{Cl}\cdot\text{H}_2\text{O}$; *chromate*, $[\text{Cr}(\text{RH})_3](\text{CrO}_4)_3\cdot 5\text{H}_2\text{O}$; *perchromate*, $[\text{Cr}(\text{RH})_3]\text{CrO}_8\cdot 4\text{H}_2\text{O}$, from (I) and H_2O_2 ; *chlorophosphate*; and *camphorsulphonate*], and which at 150—160° gives chromium trisdiguanide, $[\text{Cr}(\text{RH})_3]$. The salt-forming properties of (II) are not explained by formulæ of previous type (cf. A., 1929, 919), which are criticised; the annexed formula is proposed.



E. W. W.

Balandin multiplet hypothesis of dehydrogenation of cycloparaffins. H. S. TAYLOR (*J. Amer. Chem. Soc.*, 1938, 60, 627—632).—Published data are correlated with the hypothesis. The dehydrogenation reactions are considered from the viewpoint of equilibrium, using newer heat data. It is concluded

that dehydrogenation of *cyclopentanes* and *cycloheptanes* at 300° is thermodynamically unfavourable, whilst that of *cyclohexane* to C_6H_6 is favourable owing to resonance stabilisation of the C_6H_6 mol. The dehydrogenation data are satisfactorily explained on the basis of probable equilibria. The Balandin hypothesis is invalidated by the observation of hydrogenation of unsaturated *cyclopentenes* and *cycloheptenes* on configuratively unsuitable catalysts.

E. S. H.

Action of sulphuryl chloride on cyclohexene. H. FRIESE and D. DJIANG (Ber., 1938, 71, [B], 667—670).—Gradual addition of SO_2Cl_2 in $CHCl_3$ to *cyclohexene* (I) in Ac_2O at -10° gives *dichlorocyclohexane* (II), b.p. 70—72°/12 mm., and 2-chlorocyclohexyl acetate, b.p. 94—96°/12 mm., hydrolysed to a mixture of *cis*- and *trans*-2-chlorocyclohexanol. The relative yields depend greatly on the temp. of the reaction. In absence of solvent (I) is largely resinified by SO_2Cl_2 . With CCl_4 as diluent the proportion of (II) is increased. $AcOH$ alone is unsuitable. Boiling Ac_2O and I give *cyclohexyl acetate* in small yield. *cyclohexane*, Ac_2O , and SO_2Cl_2 give unchanged material, *chlorocyclohexane*, and resin. Cold Ac_2O and SO_2Cl_2 give a little $CH_2Cl \cdot CO_2H$ whereas the warm reactants yield $AcCl$.

H. W.

Chlorination of benzene hexachloride. T. VAN DER LINDEN (Rec. trav. chim., 1938, 57, 217—224).—Contrary to Matthews (J.C.S., 1891, 59, 165), α -benzene hexachloride with excess of liquid Cl_2 in a sealed tube slowly forms α -nonachlorocyclohexane, m.p. 95—96°, which forms mixed crystals with 1:2:4- $C_6H_3Cl_3Cl_6$ (I) and with *dechlorocyclohexane*. β -Benzene hexachloride similarly gives mainly β -*p*-dichlorobenzene hexachloride (II), with, probably, (I) (cf. Willgerodt, A., 1887, 806). Further chlorination of (II) yields an *undecachlorocyclohexane*, m.p. (indef.) 85°. γ -Benzene hexachloride similarly with at least 3 Cl gives a higher chlorinated benzene hexachloride, from which HCl is liberated easily by $MeOH \cdot NaOMe$, forming C_6Cl_6 .

A. T. P.

Reactivity of substituents in benzene derivatives. (Dipole moment, configuration of aromatic nucleus, and reactivity of substituents.) A. MANGINI (Mem. R. Accad. Ital., 1936, 7, 1—23).—Theoretical; the reactivity of C_6H_6 derivatives (especially di- and tri-substituted) is correlated with dipole moment and with the theories of Fry and of Bonino.

E. W. W.

Dipole moment, configuration, and reactivity of aromatic nitro-derivatives. A. MANGINI (Mem. R. Accad. Ital., 1936, 7, 241—276).—Theoretical; the reactivity of trihalogeno- and trinitro-benzenes, and of tetra- and penta-substituted benzenes, and substituted toluenes, is discussed (cf. preceding abstract).

E. W. W.

Alkylation of benzene by esters in the Friedel-Crafts reaction. E. BOWDEN (J. Amer. Chem. Soc., 1938, 60, 645—647).—With C_6H_6 and $AlCl_3$ the following esters give the yields of product stated: $EtOAc$ $PhEt$ (60%); Pr^iOAc $PhPr^i$ (68%); $Bu^iC_2O_4$ $CHPhMeEt$ (55%); Et_2SO_4 $PhEt$ (80%); $Bu^i_2SO_3$ $CHPhMeEt$ (41%); $Pr^i_2SO_3$ or HCO_2Pr^i $PhPr^i$ (66%); Bu^iOAc $PhBu$ (33%); HCO_2Bu^i , $EtCO_2Bu^i$,

$Pr^iCO_2Bu^i$, $Bu^iCO_2Bu^i$, $CH_2EtPr^iCO_2Bu^i$, Bu^iOBz , and Bu^i stearate $CHPhMeEt$ (73, 92, 73, 85, 78, 80, and 40%, respectively). In many cases slow addition of the ester or gradual heating is essential for good yields and sometimes the amount of $AlCl_3$ to be used is crit. The nature of the products sometimes demands and sometimes excludes formation of the olefine prior to reaction. R. S. C.

Alkylation of benzene with cycloparaffins in the presence of sulphuric acid. V. N. IPATIEV, H. PINES, and B. B. CORSON (J. Amer. Chem. Soc., 1938, 60, 577—578).—Passage of *cyclopropane* into C_6H_6 and conc. H_2SO_4 at 2—4° gives $Pr^i_2SO_4$ and $PhPr^i$, the sulphate being thus the effective reagent. *Methylcyclobutane* gives less readily *tert*-amylbenzenes; this involves the steps: $CHMe < (CH_2)_3 \rightarrow CH_2Pr^i \cdot CH_2 \cdot HSO_4 \rightarrow CHPr^i \cdot CH_2 \rightarrow CHMePr^i \cdot HSO_4 \rightarrow CMe_2 \cdot CHMe \rightarrow CMe_2Et \cdot HSO_4$, this last product being the effective reagent. *cyclopentane* does not alkylate C_6H_6 .

R. S. C.

Organic reactions with dihydroxyfluoboric acid. T. B. DORRIS, F. J. SOWA, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1938, 60, 656—657).—The catalytic activity of $BHF_2(OH)_2$ does not depend on its dissociation to BF_3 , since the latter, but not the former, catalyses reaction of $PhOH$ and Pr^iOH and since BF_3 is decomposed by the H_2O formed during esterifications whereas $BHF_2(OH)_2$ may be recovered and used again. In general BF_3 is the more powerful catalyst and more prone to cause polymerisation; $BHF_2(OH)_2$ is much less effective in rearranging $PhOPr^i$. $BHF_2(OH)_2$ causes reaction of $PhOH$ with C_3H_8 and C_4H_8 to give $PhOalk$, $C_6H_4Alk \cdot OH$, and $C_6H_4Alk \cdot Oalk$, of C_6H_6 with C_4H_8 to give *sec*-butylbenzenes, and of C_4H_8 and $AcOH$ to give $BuOAc$ (with increased branching of the Bu). With $BHF_2(OH)_2$ and MgO CH_3CBu and $MeOH$ or $CH_3 \cdot C(C_5H_{11})$ and $AcOH$ give $CMeBu^i(OMe)_2$ and $CH_2 \cdot C(C_5H_{11}) \cdot OAc$, respectively.

R. S. C.

Methylation of xylene. H. CLÉMENT and J. SAVARD (Compt. rend., 1938, 206, 610—612).—Interaction of xylene with $MeCl$ in the presence of $AlCl_3$ at 95° affords in succession $C_6H_3Me_3$, $C_6H_2Me_4$, C_6HMe_5 , C_6Me_6 . The constituents of the reaction mixture are partly separated by fractional distillation and crystallisation and, knowing the amount of HCl liberated, the quantities of the individual constituents are determined. The rate of formation of each agrees with that to be expected from successive unimol. reactions. Towards the end of the reaction the theoretical and experimental curves diverge, probably because the reaction products resinify.

J. L. D.

Methylation of xylene by the Friedel-Crafts reaction. J. SAVARD and R. HÖSÖGÜT (Rev. Fac. Sci. Istanbul, 1937, 3, 27—43).—The rates of formation of HCl and methylated products, when $MeCl$ is passed at const. rate into xylene (106 g.) and $AlCl_3$ (20 g.) at 95° for 1—26 hr., are determined. When only two org. products are formed, the amounts are calc. from the amount of HCl liberated; when >2 products are formed, one or more are isolated and the amounts of the remaining two are calc. Disappearance of xylene follows an exponential equation having

$k = 63 \times 10^{-4}$. Tri-, tetra-, penta-, and hexamethylbenzene are formed by successive reactions, $k \times 10^4$ for formation the three last-mentioned products being 50, 20, and 5, respectively. The results indicate that reaction proceeds by way of a complex, $AlCl_3 \cdot MeCl$. R. S. C.

Polymethylbenzenes. XXI. Side-chain bromination of prehnitene and some 2:3:6-trimethylphenyl derivatives. L. I. SMITH and C. L. AGRE (J. Amer. Chem. Soc., 1938, 60, 652—654; cf. A., 1938, II, 187).—XXI. Addition of Br to prehnitene at 140° in light gives 41% of 2:3:6-trimethylbenzyl bromide (I), b.p. 146°/23 mm., and some Br_2 -derivative, m.p. 205°. With $CHNa(CO_2Et)_2$ (I) gives Et_2 2:3:6-trimethylbenzylmalonate, b.p. 186—189°/10 mm., converted successively into the corresponding acid, m.p. 143—144° (decomp.), and 2:3:6-trimethylphenylpropionic acid, m.p. 91—92°. With Ac_2O and $KOAc$ in $AcOH$ (I) gives 2:3:6-trimethylbenzyl acetate, b.p. 152°/23 mm., hydrolysed to the alcohol, m.p. 83.5—85°, which is oxidised by $KMnO_4$ to 2:3:6- $C_6H_2Me_3 \cdot CO_2H$ (II), new m.p. 110—111°. Jacobsen rearrangement of 1:2:4:5- $C_6H_2Me_3Br \cdot SO_3H$ gives 1:2:4:3:5- $C_6HMe_3Br \cdot SO_3H$ [not obtainable by bromination of 1:2:4:5- $C_6H_2Me_3 \cdot SO_3H$ (cf. Smith and Moyle, A., 1936, 323)], hydrolysed by H_2SO_4 at 150° into 3-bromo-*p*-cumene, b.p. 94.5—95.5°/8 mm., which with $MgEtBr$ under N_2 affords (II). R. S. C.

Thermal polymerisation of styrene.—See A., 1938, I, 256.

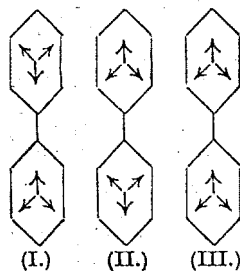
Polymerisation of styrene in heavy water and heavy alcohol. M. KOIZUMI and T. TITANI (Bull. Chem. Soc. Japan, 1938, 13, 304—305).—Styrene polymerises at 100° without exchange of H when shaken in D_2O or dissolved in $EtOD$. Polymerisation thus does not involve loosening of H. R. S. C.

Organic sulphur compounds. III. New aromatic sulphides. L. BERNERO and J. J. HERERA (IX Congr. intern. quim. pura appl., 1934, 4, 238—249).— $Ph \cdot [CH_2]_2 \cdot Cl$ (best from $Ph \cdot [CH_2]_2 \cdot OH$ and $SOCl_2$ in $PhMe$) with K_2S in $EtOH$ yields *di-β-phenylethyl sulphide*, m.p. 92°, oxidised by H_2O_2 in $AcOH$ to *di-β-phenylethyl sulphoxide*, which then passes rapidly into *di-β-phenylethyl sulphone*, m.p. 101°. *γ-Phenyl-n-propyl chloride* similarly yields *di-γ-phenyl-n-propyl sulphide*, m.p. 73°, *di-γ-phenyl-n-propyl sulphoxide*, m.p. 86—88°, and *di-γ-phenyl-n-propyl sulphone*, m.p. 117° (cf. A., 1936, 1229).

CH. ABS. (r)

Nuclear substitution in diphenyl. A. MANGINI (Mem. R. Accad. Ital., 1937, 8, 719—793).—Theoretical. On Bonino's theory, substitution reactions in substituted diphenyls will depend on a polarisation which may be "convergent" (I), "divergent" (II), or "anti-symmetric" (III). Polarisation (I) is ascribed to Ph_2 itself, and polarisations for many of its derivatives, and for fluorene and its derivatives, in different conditions, are discussed.

E. W. W.



Diphenyl and its derivatives. XVII. Passage from the diphenyl to the fluorene system: synthesis of 4-methylfluorene. L. MASCARELLI and A. ANGELETTI. XVIII. Ullmann reaction in relation to diphenyl derivatives asymmetrically substituted in the 2:2'-positions. L. MASCARELLI and B. LONGO. XIX. Preparation of some new derivatives. L. MASCARELLI and M. PRONA. XX. New example of passage from the diphenyl to the fluorene system: synthesis of 3-methylfluorene. L. MASCARELLI and B. LONGO (Gazzetta, 1938, 68, 29—32, 33—48; Atti R. Accad. Lincei, 1937, [vi], 26, 243—244, 292—297).—XVII. 6'-Nitro-6-amino-2:2'-dimethyldiphenyl (A., 1931, 1408) is diazotised and reduced ($NaHSnO_2$) to 6-nitro-2:2'-dimethyldiphenyl, m.p. 42—43°, of which the corresponding 6- NH_2 -compound, m.p. 105°, yields, on diazotisation, 4-methylfluorene, m.p. 63°, with a phenolic compound, m.p. 151—152°.

XVIII. The reactions of $PhCl$, $PhBr$, and PhI , and of 83 substituted derivatives of these (including naphthalenes), with Cu to give diphenyls are compared. *o*-Halogenonitrobenzene react with greatest facility. In a reaction such as $o-C_6H_4I \cdot NO_2 + o-C_6H_4MeCl \rightarrow 2:2'-C_6H_4Me \cdot C_6H_4 \cdot NO$, the tendency to form $2:2'-(C_6H_4 \cdot NO_2)_2$ can be overcome by using a large excess of $o-C_6H_4MeI$. The prep. of *as*-2:2'-substituted diphenyls is reviewed.

XIX. 2:2'- $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot OMe$ (I) yields (Sandmeyer) 2'-chloro-2-methoxy-, m.p. 53—54°, and (HI) 2'-amino-2-hydroxy-diphenyl (II), m.p. 92—93°, accompanied by traces of its *o*-*I*-derivative, m.p. 140°. 2:2'- $C_6H_4Cl \cdot C_6H_4 \cdot NH_2$ yields (diazotisation) 2'-chloro-2-hydroxydiphenyl (*Ac* derivative, m.p. 70°). 3:3'-($C_6H_4 \cdot NH_2$)₂ gives (Sandmeyer) 3:3'-di-iododiphenyl, m.p. 72°. Attempted prep. of 2:2'- $C_6H_4I \cdot C_6H_4 \cdot OH$ from (II), and of 2:2'- $OH \cdot C_6H_4 \cdot C_6H_4 \cdot OMe$ from (I), gave only diphenylene oxide.

XX. 6:6'-Diamino-2:2'-dimethyldiphenyl, diazotised and treated with H_2O , gives only 4:5-dimethyldiphenylene oxide (A., 1935, 757). 1:4:2- $C_6H_2Me_3I$ (improved prep.; cf. A., 1935, 1229) and $o-C_6H_4I \cdot NO_2$ give (Cu at 250—260°) 2'-nitro-2:5-dimethyldiphenyl, reduced ($SnCl_2$) to the 2'- NH_2 -compound, of which the hydrochloride is converted (diazotisation and H_2O) into 3-methylfluorene, m.p. 88—89°. E. W. W.

Synthesis of 3:4-dimethyldiphenyl. Constitution of Liebermann's benzanthrone. E. GHIGI (Ber., 1938, 71, [B], 684—689).—4-Bromo-*o*-xylene is transformed by the successive action of Mg in Et_2O and cyclohexanone into 1:3':4'-dimethylphenylcyclohexanol, which passes when distilled in a vac. or heated with $KHSO_4$, HCO_2H , or $H_2C_2O_4$ mainly into 1:3':4'-dimethylphenyl- Δ^1 -cyclohexene, b.p. 167—169°/5—6 mm. This is dehydrogenated by S at 210—220° to 3:4-dimethyldiphenyl, b.p. 281—283°, oxidised by $KMnO_4$ in presence of $MgSO_4$ to diphenyl-3:4-dicarboxylic acid, m.p. 201—202° when rapidly heated, identical with the product obtained from Liebermann's benzanthrone (A., 1938, II, 64). This acid is also obtained by the same process from the product of the successive action of H_2SO_4 and Br on *o*-xylene. It is therefore probable that 5- not 3-bromo-*o*-xylene-4-sulphonic acid is formed intermediately. H. W.

Photochemical transformations of hydrogenated naphthalene derivatives. Mechanism of photopolymerisation of acetylene. W. KEMULA and B. L. DUNICZ (Z. physikal. Chem., 1938, 181, 359—366).—Both 1:2- and 1:4-dihydronaphthalene readily yield $C_{10}H_8$ and H_2 under the total radiation from a quartz Hg lamp. Tetrahydronaphthalene is decomposed with more difficulty, giving H_2 and an unidentified product. The results support the theory previously advanced (A., 1934, 168) for the photopolymerisation of C_2H_2 . F. L. U.

Hydrogenation of 9:10:11-triphenylnaphthacene; formation of triphenyldihydronaphthacene, $C_{36}H_{26}$. M. BADOCHÉ (Bull. Soc. chim., 1938, [v], 5, 164—169).—Reduction of 9:10:11-triphenylnaphthacene (I) gives a H_2 -derivative (II), m.p. 208—209°, also obtained, with (I), by reduction of 9:10:11-triphenylnaphthacene-12-carboxylic acid or its Na salt. The addition of H is probably in a *meso*-position (cf. Dufraisse, A., 1936, 1499). Isomerides of (I) or (II) are not known and (I) shows no transformation into a ψ -form during hydrogenation. (II) is therefore probably 9:10:11-triphenyl-11:12-dihydronaphthacene. (II) is stable to light alone or in C_6H_6 , and when heated above the m.p. alone or with PbO gives (I). It does not react with HI or Na in Et_2O . E. G. B.

Perhydrophenanthrene. J. I. DENISENKO and V. M. KOTELNIKOVA (J. Gen. Chem. Russ., 1937, 7, 2819—2822).—Octahydrophenanthrene and H_2 at 180—220° (Pt- or Pd- $CaCO_3$ catalysts) yield perhydrophenanthrene, b.p. 275—276°/754.3 mm., which gives phenanthrene when passed with CO_2 over Pt-C at 300°. R. T.

Synthesis of 7-chloro-10-methyl-1:2-benzanthracene and related compounds. M. S. NEWMAN and M. ORCHIN (J. Amer. Chem. Soc., 1938, 60, 586—589).— p - C_6H_4Cl -MgBr and 1:2- $C_{10}H_6(CO_2O)$ in Et_2O - C_6H_6 give 31% of 2-*p*-chlorobenzoyl-1- (I), m.p. 191.2—191.6°, and 10% of 1-*p*-chlorobenzoyl-2-naphthoic acid (II), m.p. 254—255.6°, and 5.5% of (?) the lactone, m.p. 167.4—167.8°, of 2-*pp*-dichloro- α -hydroxybenzhydryl-1-naphthoic acid. The structure of (I) is proved by decarboxylation to *p*-chlorophenyl 2-naphthyl ketone, m.p. 125.6—126° (2:4-dinitrophenylhydrazones, forms, m.p. 237.4—238.2° and 260—261°), previously considered to be the 1- $C_{10}H_7$ ketone, but giving no benzanthrone derivative (cf. A., 1922, i, 258; 1933, 611) and obtained also from *p*- C_6H_4Cl -MgBr and 2- $C_{10}H_7$ -CN. 1- $C_{10}H_7$ -CN affords *p*-chlorophenyl 1-naphthyl ketone, b.p. 203—206°/4 mm. (2:4-dinitrophenylhydrazones, m.p. 275.4—277°), which gives 10% of 10-chlorobenzanthrone. With MgMeI (I) gives the lactone, m.p. 99.8—100.4°, of 2- α -hydroxy- α -*p*-chlorophenylethyl-1-naphthoic acid, reduced by Zn-Hg-HCl-AcOH in 70% yield to 2- α -*p*-chlorophenylethyl-1-naphthoic acid, m.p. 226—227°, which with H_2SO_4 at 15° gives the anthrone, reduced by Zn dust in NaOH to 7-chloro-10-methyl-1:2-benzanthracene (III), m.p. 164.4—164.8° (picrate, m.p. 156.4—157°). Oxidation yields 7-chloro-1:2-benzanthraquinone, m.p. 232.2—232.8°. With CuCN in C_6H_5N at 255° (III) gives 80% of the 7-CN-compound (IV), m.p. 182.5—183°, and thence 10-methyl-1:2-benzanthracene-7-carb-

oxyllic acid (V), m.p. 346—347° (uncorr.) (*Me* ester, m.p. 186.2—186.8°). When injected into mice, (III), (IV), and (V) produced no tumours in 4 months, but 5-cyano-10-methyl-1:2-benzanthracene is as active as 10-methyl-1:2-benzanthracene. M.p. are corr. M.p. of picrates are sharper and higher in Pyrex glass. R. S. C.

Selenium dehydrogenation of napelline. E. F. ROGERS and W. FREUDENBERG (Science, 1938, 87, 139).—Se dehydrogenation of napelline gives the hydrocarbon $C_{17}H_{16}$ [picrate, orange needles, m.p. 130°; $C_6H_5(NO_2)_3$ derivative, dark yellow needles, m.p. 138°] (cf. A., 1937, II, 527). L. S. T.

Many-membered ring-systems. A. MÜLLER (Österr. Chem.-Ztg., 1938, 41, 89—95).—A lecture. R. S. C.

Associating effect of the hydrogen atom.
II. Substituted anilines and related substances.
 H. O. CHAPLIN and L. HUNTER (J.C.S., 1938, 375—382; cf. A., 1937, I, 513).—Only *o*-nitroacylanilines (acyl = Ac, Bz, *p*- C_6H_4Me -SO₂) are unassociated, the *m*- and *p*-isomerides showing considerable association with increasing concn. Similar tendencies are noted where NO_2 is replaced by $N=NAr$, CO_2Et , $COMe$, and in 1-acetamidoanthraquinone. The association factors are calc. from cryoscopic measurements in $C_{10}H_8$, in which the *o*-compounds are more sol. than the *m*- and *p*-isomerides. Evidence confirming a chelate structure in the *o*-compounds is provided by wet m.p. data (cf. Baker, A., 1935, 85). Formulae for the chelated 8-acetamidoquinoline are suggested. 1:2- (I), 2:1- (II), 4:1- (III), and 8:2- NO_2 - $C_{10}H_6$ -NHAc (IV) are examined; (I) is not markedly associated, is most sol. in $C_{10}H_8$, has the lowest m.p., and shows the smallest wet m.p. depression. (II) is comparable with (III) and (IV), in which chelation is impossible. That the absence of a co-ordinated structure in (II) is due to steric interference between the Ac and the *peri*-CH group of the $C_{10}H_8$ nucleus is confirmed by a study of a no. of 6-substituted (Me, Br, NO_2) *o*-nitroacetanilides (V), where a similar steric effect obtains, tending to oppose chelation. This is interpreted as evidence of restricted rotation about the N-nuclear single linking in (V). The relatively small effect of the *o*-Br (with respect to NHAc) in *Et* 3:5-dibromo-2-acetamidobenzoate, m.p. 137°, is probably due to the stronger tendency of the CO_2Et , compared with NO_2 , to co-ordinate with H; wet m.p. data, however, point to a non-chelate structure, thus confirming the steric effect. Association-concn. curves of numerous compounds are recorded. *Et* *m*-acetamidobenzoate, m.p. 84°, is new. A. T. P.

Base strength of amine- and phosphine-oxides.—See A., 1938, I, 250.

Oxidation of mescaline and certain other amines.—See A., 1938, III, 437.

Arylamino-naphthalene derivatives.—See B., 1938, 353.

Preparation of diphenylguanidine.—See B., 1938, 353.

Reaction of diazonium salts with thiocarbamide and its derivatives. M. BUSCH and K.

SCHULZ (J. pr. Chem., 1938, [ii], 150, 173—185).—NHPH·NH·CS·NHPH reacts with PhN_2Cl in COMe_2 or $\text{COMe}_2\text{-EtOH}$ in the *iso*-form to give NHPH·NH·C(NPh)·S·N₂Ph, which decomposes spontaneously to N₂ and *S*-phenyl- α -diphenylisothiosemicarbazide, NHPH·NH·C(NPh)·SPh, m.p. 75° [hydrochloride, m.p. 205° (decomp.)]; with alkali gives NHPH·NH·CS·NHPH and PhSH, and by oxidation (? by HNO_2) anilobenzeneazophenylthiomethane, NPh·N·C(SPh)·NPh, m.p. 115°, also obtained from the former product by H_2O_2 or yellow HgO . $p\text{-NO}_2\text{·C}_6\text{H}_4\text{·N}_2\text{Cl}$ in COMe_2 gives similarly α -diphenyl-*S*-*p*-nitrophenylisothiosemicarbazide hydrochloride (I), m.p. 205° (decomp.), from which the base could not be isolated by NH_3 owing to spontaneous decomp. to $(p\text{-NO}_2\text{·C}_6\text{H}_4\text{·S})_2$. (I) reacts as NHPH·NH·C(NPh)·S·C₆H₄·NO₂ with HgO since it yields anilobenzeneazo-*p*-nitrophenylthiomethane, m.p. 118°, but with CH_2O or PhCHO in EtOH it reacts in the tautomeric form yielding 1:4-diphenyl-, m.p. 127°, and 1:4:5-triphenyl-3-*p*-nitrophenylthiol-4:5-dihydro-1:2:4-triazole, m.p. 124° (hydrolysed by warm dil. H_2SO_4), respectively. CS(NHPH)_2 does not react with PhN_2Cl , but with $p\text{-NO}_2\text{·C}_6\text{H}_4\text{·N}_2\text{Cl}$ affords NN'-diphenyl-*S*-*p*-nitrophenylisothiocarbamide, m.p. 131°, which is very readily hydrolysed to $\text{NO}_2\text{·C}_6\text{H}_4\text{·SH}$ (or its disulphide) and CO(NHPH)_2 . *N*-Phenyl-*N'*-*p*-bromophenyl-*S*-*p*-nitrophenylisothiocarbamide, m.p. 158°, is similarly obtained. $\text{CS(NH}_2)_2$ and PhN_2Cl give the unstable azo-compound, $\text{NH}_2\text{·C(NH)·S·N}_2\text{Ph}$, which decomposes in EtOH into formamidine disulphide dihydrochloride, m.p. 173—174° (decomp. from 170°), PhSH, and other products. Similarly is obtained the slightly more stable azo-compound, $\text{NH}_2\text{·C(NH)·S·N}_2\text{·C}_6\text{H}_4\text{·NO}_2$ -*p* (hydrochloride), which in EtOH decomposes partly by oxidation of the EtOH yielding PhNO_2 , N₂, and $[\text{NH}_2\text{·C(NH)·S}]_2$, and partly by loss of N₂ and hydrolysis of the $\text{NH}_2\text{·C(NH)·S·C}_6\text{H}_4\text{·NO}_2$ produced to $\text{CO(NH}_2)_2$ and $\text{NO}_2\text{·C}_6\text{H}_4\text{·SH}$. NHPH·CS·OEt and PhN_2Cl do not react, but $p\text{-NO}_2\text{·C}_6\text{H}_4\text{·N}_2\text{Cl}$ in COMe_2 gives $\text{NO}_2\text{·C}_6\text{H}_4\text{·N}_2\text{·S·C(OEt)·NPh}$, which decomposes at once into N₂ and $p\text{-NO}_2\text{·C}_6\text{H}_4\text{·SH}$; excess of $\text{NO}_2\text{·C}_6\text{H}_4\text{·N}_2\text{Cl}$ then leads to *p*-nitrobenzeneazothioli-*p*-nitrobenzene (II), $\text{NO}_2\text{·C}_6\text{H}_4\text{·N}_2\text{·S·C}_6\text{H}_4\text{·NO}_2$, decomp. 142°, also obtained similarly from NHPH·CS·OMe or $\text{CH}_2\text{·CH·CH}_2\text{·NH·CS·OEt}$. NHPH·CS·O·CH₂Ph, however, in C_6H_6 gives by coupling, loss of N₂ and CH_2Ph , *S*-*p*-nitrophenyl thiocarbaniolate, m.p. 158°; in $\text{COMe}_2\text{-EtOH}$ N₂, $(\text{NO}_2\text{·C}_6\text{H}_4\text{·S})_2$ (by oxidation), (II), and a *S*-containing substance, m.p. 204°, are obtained. R. S. C.

Phosphoryl chloride as a condensing agent in the preparation of amidines from acylamines. M. M. SIDIKI and R. C. SHAH (J. Univ. Bombay, 1937, 6, Part II, 132—133).— POCl_3 is an efficient condensing agent in the prep. of diphenyl-cinnamidine, m.p. 123°, -crotonamidine, m.p. 85°, acetamidine, and benzamide from NH_2Ph and the respective anilides. F. R. S.

Derivatives of *N*-phenylbenzamidine. I. H. P. GHADIALI and R. C. SHAH (J. Univ. Bombay, 1937, 6, Part II, 127—131).—*N*-Phenylbenzamidine (I), new m.p. 115—117°, is best obtained from $\text{Et}_2\text{O-}$

CPhCl·NPh and a large excess of MeOH-NH_3 ; with less NH_3 , a compound, probably $\text{NPh·CPh·NPh·CPh·N·CPh·NPh}$, m.p. 176—178° (hydrochloride, m.p. 244—246°), is also formed. From (I) are obtained Bz_2 , m.p. 143°; and Bz_1 derivative, m.p. 143° (cf. Wheeler *et al.*, A., 1903, i, 858); the latter could not be cyclised to a quinazoliné. CPhCl·NPh with the Na derivative of NH_2Bz affords a compound, probably NBz(CPh·NPh)_2 , m.p. 171—172°, or diphenylbenzamidine, according to the conditions used. F. R. S.

Reactions of oxanilidedi-imidochloride (diphenyloxalimidochloride). V. R. HEERAMANICK and R. C. SHAH (J. Univ. Bombay, 1937, 6, Part II, 80—81).—Oxanilidedi-imidochloride (I), NPhEt_2 , and NH_2Ph give tetraphenyloxalamidine, m.p. 156—158° (lit. 153°) (dihydrochloride, m.p. 242°). NaOEt and (I) in PhMe afford Et_2 di(anilo)oxalate, m.p. 42° (lit., b.p. 205°/12 mm.); NaOPh similarly forms Ph_2 di(anilo)oxalate, m.p. 130—132°. F. R. S.

Manufacture of polyamines.—See B., 1938, 353.

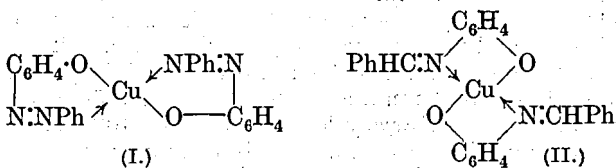
Action of hydrazine on *o*-, *m*-, and *p*-nitrotoluene in presence of sodium ethoxide. B. M. BOGOSLOVSKI and A. S. TSCHERNISCHEV (J. Gen. Chem. Russ., 1937, 7 2779—2782).— $p\text{-C}_6\text{H}_4\text{Me·NO}_2$ in EtOH-NaOEt and N_2H_4 (10 min. at 100°) yield an inseparable mixture, m.p. 245—260°, of bisazoxy- and azoazoxy-distilbene, together with 4:4'-dinitro-dibenzyl and 4:4'-azoxytoluene. Under similar conditions *o*- and *m*- $\text{C}_6\text{H}_4\text{Me·NO}_2$ afford 2:2'- and 3:3'-azoxytoluene, respectively. R. T.

Stereoisomeric forms of azobenzene. K. VON AUWERS (Ber., 1938, 71, [B], 611—612).—The differences between *n* of the two forms of azobenzene exceed those between the stereoisomeric azoxybenzenes and correspond with those of the two stilbenes. Hartley's conception of the *cis* nature of his compound (A., 1937, II, 454) is thus confirmed spectrochemically. H. W.

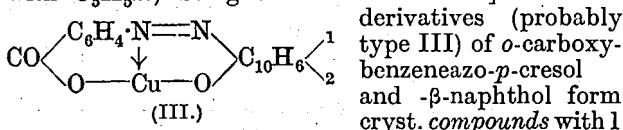
Azo-chromophore. VII. J. S. P. BLUMBERGER (Chem. Weekblad, 1938, 35, 227—235).—Spectroscopic investigations are described on chromophore inversion (hypsochromic colour change with OH^-) with a no. of naphthaleneazo-dyes containing OH groups in the *peri*-position, and with dyes derived from *p*-cresol, pyrazolones, acetoacetanilides, and 1:8- $\text{C}_{10}\text{H}_6(\text{OH})_2$. Inversion occurs in every case where a subsidiary valency can be visualised between the azo- and the OH groups. In monoazo-dyes containing OH groups in both the *o*-position to the azo-group and in the *peri*-position, only one of these groups shows a hypsochromic change due to inversion and the other a bathochromic change, both of which are easily observed. Inversion occurs with dyes derived from pyrazolones, acetoacetanilide, and $\text{CH}_2\text{Ac·CO}_2\text{Et}$. Unexpectedly, *o*-hydroxyazo-dyes from *p*-cresol show no inversion whilst 2-hydroxy-naphthalene-3-azo-dyes show the effect only slightly in *zp*. cases. These dyes are not constituted like a "zwitterion" (cf. Bergmann and Weizmann, A., 1936, 1183). S. C.

Structure of the copper lakes of azo-dyes. H. D. K. DREW and J. K. LANDQUIST (J.C.S., 1938,

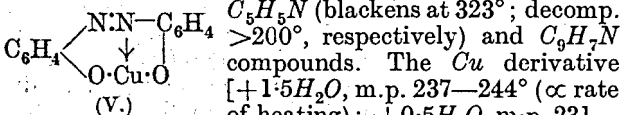
292—304).—The structures and stereochemical forms of the Cu lakes, of, e.g., *o*-OH-, *o*-CO₂H-, *oo'*-(OH)₂-*o*-hydroxy-*o'*-carboxy-, and *oo'*-(CO₂H)₂-azo-compounds of C₆H₆ and C₁₀H₈ series are discussed. Examples are given of lakes in which one OH is *m*- or *p*- to ·N·N·; also of *o*-hydroxyazo-sulphonic acids. The Cu lakes of *o*-hydroxy- (I), m.p. 223°, 2-hydroxy-5-methyl-, m.p. 232°, 2-hydroxy-5 : 5'-dimethyl-, m.p. 225°, -azobenzene, and of benzene-, m.p. 292°, and



m-toluene-, m.p. 240—241°, -azo-β-naphthol, are all anhyd., are co-ordinatively saturated, and do not affix further mols. of bases. The Cu atom cannot be co-ordinated with both N of one ·N·N·, and formulæ (type I) with *anti*-azo-groups and Cu attached to N remote from OH are preferred to alternatives (*syn*- and *anti*-), where Cu is attached to N adjacent to OH; the latter are not strictly excluded, as e.g., the Cu derivative of *o*-OH·C₆H₄·N:CHPh is possibly (II). Azobenzene-*o*-carboxylic acid forms a Cu salt [+2H₂O, m.p. 141—144°; +2NH₂Ph, m.p. 142°; +3C₅H₅N, m.p. 145—148° (decomp.); +0.5C₅H₅N, m.p. 183—184° (decomp.); +2C₅H₅N; +COMe₂, m.p. 142° (decomp.)], and the possible formulæ of the anhyd. derivative, m.p. 120—126° (decomp.) (impure), are discussed. Azobenzene-2 : 2'-dicarboxylic acid forms a Cu salt [probably +2H₂O; 1 H₂O is retained at 110°, the *monohydrate* (forms unstable compounds with C₅H₅N) being stable in moist air]. The Cu



derivatives (probably type III) of *o*-carboxybenzeneazo-*p*-cresol and -β-naphthol form *cryst. compounds* with 1 mol. of NH₂Ph or C₅H₅N. Na benzeneazo-β-naphthol-3'-carboxylate with CuCl₂ gives a Cu derivative (not pure) (1 Cu : 2 azo-compound), which separates from C₅H₅N in two forms (both +2C₅H₅N), m.p. 233—234° and 115—120°, decomposed by H₂O (formulae suggested), and from NH₂Ph with 3 or 4 mols., 2 more firmly combined. Benzeneazo- α -naphthol-2'-carboxylic acid yields a Cu derivative, +2H₂O (IV) (1 Cu : 2 azo-compound) [*anhyd.* from hot NH₂Ph; (C₅H₅N)₂ compound, which with boiling H₂O gives the *trihydrate*, converted into (IV) at 105°]. The *p*-OH thus appears to take no part in the fixation of Cu. 2 : 2'-Dihydroxyazobenzene and *o*-hydroxybenzeneazo-β-naphthol give Cu derivatives (probably type V), m.p. 346—347° (decomp.) and >365°, respectively, co-ordinatively unsaturated, yielding C₅H₅N (blackens at 323°; decomp. >200°, respectively) and C₆H₇N compounds. The Cu derivative [+1.5H₂O, m.p. 237—244° (\propto rate of heating); +0.5H₂O, m.p. 231—233°] of *m*-hydroxybenzeneazo-β-naphthol (1 Cu : 2 azo-) behaves differently from that of *oo'*-dihydroxyazo-compounds, only the *o*-OH being involved. The



F** (A., II.)

Cu salt of salicylidene-*o*-aminophenol resembles type (V).

Azobenzene-4-sulphonic acid forms a Cu salt [*penta-hydrate*; +3C₅H₅N; +? 5 or 6C₅H₅N]; its properties suggest that, in solution, Cu is feebly co-ordinated with ·N·N·, but when cryst. the union is probably disrupted, being replaced by co-ordination with H₂O or bases. Strongly hydrated Cu salts of 2-hydroxy-5-methylazobenzene-3'- (+7H₂O) and -4'- (+6 or 7H₂O; +3H₂O; NH₄ Cu salt) -sulphonic acid, benzeneazo-β-naphthol-4'-sulphonic acid (VI) (+7H₂O; +2H₂O; +2C₅H₅N, 5H₂O; +4C₅H₅N, 3H₂O), 2-hydroxy- α -azonaphthalene-4'-sulphonic acid (+7 or 8H₂O), and benzeneazo-β-naphthol-8- (+4H₂O; +4C₅H₅N) and -6 : 8-di- (+8H₂O; Ba salt +8H₂O) -sulphonic acids are described; salt formation occurs at the SO₃H, the OH being free. In presence of alkali or metal acetates they are converted into complexes in which Cu atoms are associated with O of the OH and with N of the ·N·N· instead of with SO₃H; e.g., the Cu salt of (VI) and NaOAc, NaHCO₃, NH₄OAc, or Cu(OAc)₂ give complexes with Na₂ or (NH₄)₂ (+6H₂O) or Cu (+6H₂O or +2C₅H₅N, 5H₂O). Similar inner-complex Cu derivatives of other *o*-hydroxyazo-sulphonic acids were obtained. 4-Sulphonaphthalene-1 : 2-diazo-oxide yields a Cu salt (+6H₂O); attempts to bring about inner co-ordination of the metal were unsuccessful.

A. T. P.

Diazotisation of picramide. W. C. LOTHROP (J. Amer. Chem. Soc., 1938, 60, 725—726).—The coupling product of β-C₁₀H₇·OH and diazotised picramide reported by de Milt and van Zandt (A., 1936, 1502) is the 1 : 1 mol. compound of picramide (I) and β-C₁₀H₇·OH. Their conditions for diazotisation are thus ineffective for (I).

R. S. C.

Phenolic compounds containing a chloromethyl group and nitrogen-containing condensation products therefrom.—See B., 1938, 354.

Polymerisation of methylchavicol. J. M. VAN DER ZANDEN (Rec. trav. chim., 1938, 57, 233—247).—Methylchavicol, *p*-OMe·C₆H₄·CH₂·CH·CH₂, heated at 250° (sealed tube) for 100 hr. (70% unchanged) to 440 hr. (20%), gives three *dimerides*, m.p. 93° (I), m.p. 166° (cf. van Romburgh, A., 1909, i, 597), and m.p. 46—47°, and a *trimeride*, m.p. 135—135.5°. Oxidation (KMnO₄, COMe₂) of (I), shown to be α -di-*p*-anisyl- Δ^a -hexene, gives anisic acid and δ -*p*-anisyl-*n*-valeric acid (II), m.p. 114—114.5°; (II) is oxidised (Kiliani) to γ -*p*-anisyl-*n*-butyric acid (III), m.p. 139.5—140.5° (*p*-nitro-, m.p. 199—200°, and 2 : 4-dinitro-phenylhydrazones, m.p. 142.5°). Et β -anisylpropionate or *p*-methoxycinnamate with Na in EtOH-PhMe gives γ -*p*-anisylpropyl alcohol, converted by PBr₃ into the *bromide*, b.p. 134—136°/10 mm., which with CHNa(CO₂Et)₂ affords Et (γ -*p*-anisylpropyl)malonate, b.p. 210—215°/1 mm., which leads to (II). (III) is synthesised from glutaric anhydride, PhOMe, and AlCl₃ at -10° to 0°. The *oxime*, m.p. 97—97.5°, of (III) and PCl₅ in Et₂O at -10° to 0° yield *N*-*p*-anisylglutarimide, m.p. 172—172.5° (also synthesised from *p*-anisidine and glutaric acid), hydrolysed by aq. EtOH-Na₂CO₃ to *N*-*p*-anisylglutaramic acid, m.p. 146—147°. Reduc-

tion (H_2 , Pd, AcOH) of (I) gives α , α -di-*p*-anisylhexane, m.p. 71.5–72°, synthesised from Na and γ -*p*-anisylpropyl bromide. A. T. P.

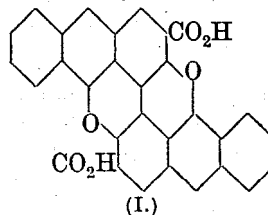
Reduction of derivatives of anhydro-2- $\beta\beta\beta$ -trichloro- α -hydroxyethoxy-1- $\beta\beta\beta$ -trichloro- α -hydroxyethylbenzene. A. N. MELDRUM and A. S. TATA (J. Univ. Bombay, 1937, 6, Part II, 120–122).—Anhydro-5-carbamyl-2- $\beta\beta\beta$ -trichloro- α -hydroxyethoxy-1- $\beta\beta\beta$ -trichloro- α -hydroxyethylbenzene, $CCl_3\cdot CHO$, and a little conc. H_2SO_4 at 100° give anhydro-5- $\beta\beta\beta$ -trichloro- α -hydroxyethylcarbamyl-2- $\beta\beta\beta$ -trichloro- α -hydroxyethoxy-1- $\beta\beta\beta$ -trichloro- α -hydroxyethylbenzene, m.p. 168° (Ac derivative, m.p. 220–222°), reduced (Zn–AcOH) to 2-hydroxy-5- $\beta\beta$ -dichlorovinylcarbamyl- $\beta\beta$ -dichloroethylbenzene, m.p. 150–152° (Ac derivative, m.p. 155–156°). Anhydro-2- $\beta\beta\beta$ -trichloro- α -hydroxyethoxy-1- $\beta\beta\beta$ -trichloro-2-hydroxyethylbenzene-5-sulphonic acid [$Na (+3H_2O)$, $K (+H_2O)$, and Ca salts ($+4H_2O$)], gives the sulphonamide, which is reduced (Zn–AcOH) to 4-hydroxy-3- $\beta\beta$ -dichloroethylbenzenesulphonamide, m.p. 181–184° (Ac derivative, m.p. 140°), and which with $CCl_3\cdot CHO$ forms anhydro-2- $\beta\beta\beta$ -trichloro- α -hydroxyethoxy-1- $\beta\beta\beta$ -trichloro- α -hydroxyethylbenzene-5- $\beta\beta\beta$ -trichloro- α -hydroxyethylsulphonamide, m.p. 194–195° (Ac derivative, m.p. 159°).

F. R. S.

Selective hydrogenation of derivatives of naphthalene and diphenyl. D. M. MUSSER and H. ADKINS (J. Amer. Chem. Soc., 1938, 60, 664–669).—The mono- and di-cyclic hydrogenation (Ni and Cu–Cr) of naphthols and hydroxydiphenyls is investigated. In presence of Raney Ni at 100°/100–200 atm. $C_{10}H_8$ is hydrogenated to tetra- and then to deca-hydronaphthalene. In presence of Cu–Cr at 200° $C_{10}H_{12}$ only is formed and more slowly. Naphthols are rapidly hydrogenated at 200° in presence of Cr–Cu, but only at 150° in presence of Ni. With Ni α - $C_{10}H_7\cdot OH$ gives 5 parts of 5 : 6 : 7 : 8- (I) to 3 parts of 1 : 2 : 3 : 4- H_4 -compound (II), some decahydro- α -naphthol, and tetrahydronaphthalene [from (II) by substitution of H for OH]. With Cr–Cu, however, 2 parts of (II) are formed to 1 part of its isomeride; in rapid reactions at 300–350 atm. much (II) is obtained. Both catalysts favour 1 : 2 : 3 : 4-reduction of β - $C_{10}H_7\cdot OH$, an 87% yield being obtained with Cu–Cr. Naphthol ethers are not hydrogenated in presence of Cu–Cr unless the temp. is so high that reduction of OR occurs; with Ni mainly (up to 80%) 5 : 6 : 7 : 8- H_4 -ether is obtained from 1- $C_{10}H_7\cdot OAlk$, but 2- $C_{10}H_7\cdot OAlk$ yield only the 1 : 2 : 3 : 4- H_4 -derivatives. With Ni *p*- $C_6H_4Ph\cdot OH$ and its ethers are preferentially hydrogenated in the unsubstituted Ph, but with *o*- and *m*- $C_6H_4Ph\cdot OH$ the reverse is the case; both rings are equally attacked in *m*- $C_6H_4Ph\cdot OEt$. With Cu–Cr the ratio is reversed for *p*- $C_6H_4Ph\cdot OH$. In general Cu–Cr favours hydrogenation of the phenolic ring, possibly because the phenol reacts in the ketonic form. The loss of OH is much less in the diphenyl series and most for α - $C_{10}H_7\cdot OH$, which is regarded after reduction as a substituted $CH_2Ph\cdot OH$. Hydrogenation of $PhOAlk$ is not prevented if Alk has a high mol. wt., although a higher temp. may be required. The methods often have a preparative val. The following are incidentally pre-

pared: 4-methoxy-1-methylcyclohexane, b.p. 149–153°/741 mm.; cyclohexyl, b.p. 153–154°/3 mm., α - $C_{10}H_7$, b.p. 210–211°/3 mm., 5 : 6 : 7 : 8-tetrahydro- α -naphthyl, b.p. 204–207°/3 mm., 1 : 2 : 3 : 4-tetrahydro- β -naphthyl, b.p. 205–207°/4 mm., and β - $C_{10}H_7$ dodecyl ether, b.p. 225–228°/4 mm., m.p. 48–49°; 4-methylcyclohexyl, b.p. 184–186°/3 mm., cyclohexyl, b.p. 188–190°/2 mm., 2-, b.p. 258–261°/3 mm., m.p. 41–42°, and 4-diphenyl, b.p. 253–255°/3 mm., m.p. 88–89°, *p*-tolyl, b.p. 199–201°/2 mm., m.p. 43–44°, 4-cyclohexylphenyl, b.p. 240–243°/2 mm., m.p. 57–58°, and 2-phenylcyclohexyl cetyl ether, b.p. 225–227°/2 mm., m.p. 29–30°; 2-phenylcyclohexyl Et, b.p. 110–113°/4 mm., and Me ether, b.p. 105–107°/3 mm.; 2-cyclohexylcyclohexyl Et, b.p. 109–110°/4 mm., and Me ether, b.p. 103–106°/4 mm.; 4-cyclohexylcyclohexyl Et, b.p. 115–116°/4 mm., and Me ether, b.p. 105–108°/4 mm.; 2-ethyl-1 : 2 : 3 : 4-tetrahydro- α -naphthol, b.p. 120–121°/2 mm.; 3-phenylcyclohexyl, b.p. 100–101°/1 mm., and 4-diphenyl Et ether, b.p. 185–188°/14 mm., m.p. 73–74°; 3-cyclohexylphenyl Me ether, b.p. 105–106°/1 mm.; 2-phenyl-4-ethylcyclohexanol, b.p. 134–136°/3 mm.; 1-ethyl-1 : 2 : 3 : 4-tetrahydro- β -naphthol, b.p. 128–129°/2 mm., m.p. 88–89°. R. S. C.

Diaryls and their derivatives. XVIII. Oxidation of 2 : 2'-dihydroxyanthracene-3-carboxylic acid. J. S. JOFFE and R. A. STOCKHAMMER. XIX. Reaction of 2-hydroxyanthracene with ferric chloride. J. S. JOFFE and L. S. EFROS. XX. Mechanism of reaction of β -naphthol and its derivatives with ferric salts. J. S. JOFFE (J. Gen. Chem. Russ., 1937, 7, 2710–2711, 2712–2714, 2715–2718).—XVIII. 2-Hydroxyanthracene-3-carboxylic acid in aq. AcOH and Fe alum (3–4 hr. at the b.p.) yield 2 : 9'-9 : 2'-dioxido-1 : 1'-dianthrylene-3 : 3'-dicarboxylic acid (I), m.p. >350° (decomp.).



XIX. 2-Hydroxyanthracene in aq. EtOH and $FeCl_3$ yield 2 : 2'-dihydroxy-9 : 9'-dianthra-10 : 10'-dione.

XX. The reaction between $FeCl_3$ and β - $C_{10}H_7\cdot OH$ (I) is represented: $(I) + FeCl_3 \rightarrow C_{10}H_7\cdot O\cdot FeCl_2$ (II) $\rightarrow (C_{10}H_7\cdot O)_2FeCl$ (III) $\rightarrow Fe(C_{10}H_7\cdot O)_3$ $\rightarrow [Fe(C_{10}H_7\cdot O)_4] \rightarrow (C_{10}H_6\cdot OH)_2$ (IV); (II) $\rightarrow C_{10}H_6Cl\cdot OH$; (III) \rightarrow (IV). R. T.

Nuclear condensation products of chloral with phenols. A. N. MELDRUM and K. V. LONKAR (J. Univ. Bombay, 1937, 6, Part II, 116–119).—Condensation (method: Pauly and Schanz, A., 1923, i, 564) of the appropriate phenol with $CCl_3\cdot CHO$ gives the following: *p*-hydroxy-($\beta\beta\beta$ -trichloro- α -hydroxyethyl)benzene [Ac_3 , m.p. 155°, Bz_3 , m.p. 132°, and Me_3 , b.p. 185°/25 mm., derivatives, reduced (Zn, AcOH) to the Ac, b.p. 190°/50 mm., Bz , m.p. 114°, and Me derivative, b.p. 187°/30 mm., of *p*-hydroxy-($\beta\beta$ -dichloroethyl)benzene; 4-methoxy-($\beta\beta$ -dichloro- α -methoxyethyl)benzene has b.p. 181°/50 mm.]; 2 : 4-dihydroxy-($\beta\beta\beta$ -trichloro- α -hydroxyethyl)benzene [Ac_3 , m.p. 132°, Bz_3 , m.p. 142°, and Me_3 derivatives, m.p. 126°; 2 : 4-diacetoxy-($\beta\beta$ -dichloroethyl)benzene has m.p. 67°]; 2 : 4-dihydroxy-1 : 5-di-($\beta\beta\beta$ -trichloro- α -hydroxy-

ethyl)benzene, m.p. 172° [*Ac*₄, m.p. 192°, and *Bz*₄ derivative, m.p. 190°, reduced to the *Ac*₂, m.p. 112°, and *Bz*₂, m.p. 138°, derivatives of 2:4-dihydroxy-1:5-di-(ββ-dichloroethyl)benzene]; 4-hydroxy-3-methoxy-(ββ-trichloro-α-hydroxyethyl)benzene (*Me*₂ derivative, b.p. 220°/10 mm.); and 2-hydroxy-5-methyl-(ββ-trichloro-α-hydroxyethyl)benzene (I) (*Ac*₂, m.p. 106°, *Bz*₂, m.p. 139°, and *Me*₂ derivatives, m.p. 104°). (I) and aq. 20% NaOH yield 1:1-dichloro-2-hydroxy-4-methyl-1:2-dihydrocoumarone (+EtOH), m.p. 182°. *p*-C₆H₄Me·OMe and CCl₃·CHO give ααα-trichloro-ββ-di-(4-methoxy-*m*-tolyl)ethane, m.p. 161°, reduced (Zn-AcOH) to αα-di-(4-methoxy-*m*-tolyl)ethane, b.p. 185°/10 mm. The *K* salt, m.p. 79°, and *Ac*, m.p. 75°, *Bz*, m.p. 95°, and *Me*, b.p. 197°/50 mm., derivatives of 4-hydroxy-3-methoxy-(ββ-dichloroethyl)benzene are described. 3:4-Dimethoxy-(ββ-dichloro-α-methoxyethyl)benzene has b.p. 140°/5 mm. F. R. S.

Hexylpyrocatechol.—See B., 1938, 456.

Toxic principle of the fruits of *Renghas* (*Semecarpus heterophylla*, Bl.). H. J. BACKER and N. H. HAACK (Rec. trav. chim., 1938, 57, 225—232).—Extraction with EtOH gives *renghol* (I), b.p. 170—172°/0.0001 mm., m.p. 14—15° (*H*₂-derivative, m.p. 58.5—59°), which is *o*-2:3-dihydroxyphenyl-Δ^α-pentadecene (cf. urushiol; Majima, A., 1922, i, 262, 263; Hill *et al.*, A., 1935, 246). Reduction of the *Me*₂ ether, b.p. 226°/5 mm., of (I) with H₂ + Pt-black in AcOH gives dimethyldihydrorenghol, m.p. 36.5—37°, identical with 2:3-dimethoxy-*n*-pentadecylbenzene (II). The carbinol from *o*-veratraldehyde and Mg tetradecyl bromide is dehydrated when distilled, to 2:3-dimethoxy-*n*-Δ^α-pentadecylbenzene, m.p. 36.5—37°, converted by H₂ + Pt-black in EtOH into (II). Decomp. of the ozonide of (I) with H₂O gives valeraldehyde (2:4-dinitrophenylhydrazones, new m.p. 106.5—107°), proving the position of the double linking in (I).

A. T. P.

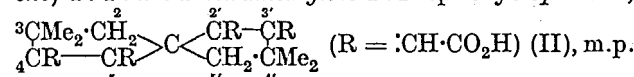
Derivatives of 1:2:3:4-tetrahydroxybenzene. IV. Attempted syntheses. W. BAKER and (Miss) C. EVANS (J.C.S., 1938, 372—375).—Intermediates are described which cannot be used successfully for preparing derivatives of 1:2:3:4-C₆H₂(OH)₄. Phenols are not obtained either from 2:5-dimethoxybenzenesulphonic acid (+2H₂O) [from *p*-C₆H₄(OMe)₂ and conc. H₂SO₄ at 60°/5 min.] or 2:5-(OMe)₂C₆H₃·NH₂ by KOH or the diazo-reaction, respectively. H₂O₂ and 2:3-dihydroxy-4-methoxybenzaldehyde, m.p. 69.5°, b.p. 172—178°/14 mm. [from 1:2:3-OMe·C₆H₃(OH)₂, Zn(CN)₂, and HCl in Et₂O], do not react. 2:3:4-(OH)₂C₆H₂(OMe)·COMe (I) and CH₂PhCl·K₂CO₃ in PhMe yield 2-hydroxy-3-benzoyloxy-4-methoxyacetophenone, m.p. 79—80°. Reduction of 5-nitro-2-methoxyphenyl acetate with H₂-Pd-SrCO₃ gives the 5-NH₂-compound (*Ac* derivative, m.p. 156—157°), converted by the diazo-reaction into 2:4-(OH)₂C₆H₃·OMe (II). CH₂Ac·CO₂Et, conc. H₂SO₄, and (II) at 0° give 7-hydroxy-6-methoxy-4-methylcoumarin (III) (4-methylscopoletin), m.p. 213.5°; its *Ac* derivative, m.p. 188—189°, and AlCl₃ at 170° yield the 8-*Ac* derivative, m.p. 250° (decomp.; previous softening), of (III), hydrolysed, however, to (II). (I) and CH₂SO₄ in COMe₂-aq. KOH yield 4-methoxy-2:3-methylenedioxyacetophenone, m.p. 102.5°; the oxime, m.p. 148.5°,

and PCl₅-Et₂O give 4-methoxy-2:3-methylenedioxyacetanilide, m.p. 138—139°.

The *Ac* derivative, m.p. 44°, of 4-hydroxyveratrole (improved prep.) and Br in AcOH-Ac₂O give 5-bromo-4-acetoxyveratrole (IV), m.p. 67°, which with KOH-Me₂SO₄ yields 5:1:2:4-C₆H₂Br(OMe)₃ (V). The *Ac* group in (IV) did not migrate with AlCl₃, neither could a new *Ac* be introduced into position 3. (V) and AlCl₃ with or without AcCl in PhNO₂ or Et₂O give 2:3:5:2':3':5'-hexamethoxydiphenyl.

A. T. P.

Condensation products of phenols and ketones. II. Pyrocatechol and acetone. W. BAKER and J. C. MCGOWAN (J.C.S., 1938, 347—353).—The condensation product, C₂₁H₂₄O₄, of *o*-C₆H₄(OH)₂ and COMe₂ in AcOH-HCl is shown to be 5:6:5':6'-tetrahydroxy-3:3:3':3'-tetramethylbis-1:1'-spirohydrindene (I) (see A., 1935, 80), the only points not established absolutely being the positions of the OH groups. Oxidation (aq. KMnO₄) of (I) and treatment of the product with Ac₂O gives some phoronic anhydride. 4 H are instantaneously replaced in (I) by Br (in AcOH); similarly 5:6-dihydroxyhydrindene (5:6-hydrindenequinone, m.p. 87°, by Ag₂O-Na₂SO₄ in Et₂O) yields the 4:7-Br₂-derivative, m.p. 95° (previous softening). By aerial oxidation in aq. NaOH for 50 hr., (I) takes up 4 O to give C₁₇H₂₀(CO₂H)₄, which, if the OH in (I) are as indicated, is 2:3:2':3'-tetra(carboxymethylene)-4:4:4':4'-tetramethylbis-1:1'-spirocyclopentane,



~260° (CO₂ evolved); it is stable to Br in AcOH or Ac₂O and is oxidised, as (I), to phoronic anhydride, and reduced by Na-Hg to 4:4:4':4'-tetramethylbis-1:1'-spirocyclopentene-2:3:2':3'-tetra-acetic acid (III), m.p. ~260° (decomp.) (*Me*₄, b.p. 195°/0.36 mm., 202°/0.53 mm., and *Et*₄ ester, b.p. 243°/2 mm.). The Ca and Ba salts of (II) and (III) are more sol. in cold than hot H₂O. When heated, (III) loses 4CO₂ to give 2:3:4:4:2':3':4':4'-octamethylbis-1:1'-spirocyclopentene (IV), b.p. 130—131°/18 mm., 250°/760 mm., which absorbs Br but is not reduced with H₂ and PdCl₂ or Pd-SrCO₃ or PtO₂, thus supporting the structure assigned and hence (I). 4:7:4':7'-Tetra-bromo-5:6:5':6'-tetramethoxy-3:3:3':3'-tetramethylbis-1:1'-spirohydrindene, m.p. 205°, is prepared by methylation of the (OH)₄-derivative (*loc. cit.*). Crystallographic examination of the dimorphic forms of the *Me*₄ ether of (I) is described. Hydroxyquinol and *m*-cresol yield derivatives of 4:4:4':4'-tetramethylbis-2:2'-spirochroman, and pyrogallol yields a 3:3:3':3'-tetramethylbis-1:1'-spirohydrindene.

A. T. P.

Pentahydroxybenzene series. II. Attempts to prepare pentahydroxytoluene derivatives from derivatives of tetrahydroxytoluene. G. AULIN and H. ERDTMAN (Svensk Kem. Tidskr., 1938, 50, 42—50; cf. A., 1937, II, 455).—The compounds previously considered to be 2:3:5-triacetoxy-4-methoxy- and 2:3:4:5-tetramethoxy-toluene are really 2:3:6-triacetoxy-4-methoxy- (I) and 2:3:4:6-tetramethoxy-toluene (II), and the data of Konya (A., 1900, i, 545) and Pollak *et al.* (A., 1902, i, 148) need revision. Homoveratrol, prepared from 1:3:4-C₆H₃Me(OH)₂

and Me_3SO_4 or by Clemmensen reduction of 3:4-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CHO}$, is nitrated to give the 6- NO_2 -derivative, which by reduction with Sn-HCl and subsequent oxidation by FeCl_3 gives 85% of 4-methoxytolu-2:5-quinone (III), m.p. 170—172°. Toluquinone, prepared from $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ and $\text{Na}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ at 10—15°, is converted into 1:2:4:5- $\text{C}_6\text{H}_2\text{Me}(\text{OAc})_3$, which, when boiled with $\text{H}_2\text{SO}_4\text{-MeOH}$ and then treated at 45° with $\text{Me}_2\text{SO}_4\text{-NaOH}$, gives 90—95% of 1:2:4:5- $\text{C}_6\text{H}_2\text{Me}(\text{OMe})_3$; this is quantitatively converted by CrO_3 in $\text{AcOH-H}_2\text{SO}_4$ into (III), which affords successively (I) and (II). $\text{CrO}_3\text{-AcOH}$ at 0° converts (II) into 2:4-dimethoxytolu-3:6-quinone (IV), m.p. 125—126.5°, also obtained (Raistrick) from 2-methoxytoluquinone by way of 3:4:6-triacetoxy-2-methoxytoluene and 4-hydroxy-2-methoxytoluquinone. In attempts to nitrate (II), it was only oxidised to (IV) with a small amount of an unstable substance containing N. Thiele-acetylation of (IV) gave a coloured solution, from which only unchanged (IV) was recovered. Hydrolysis of (I) and oxidation by FeCl_3 gives 2-hydroxy-4-methoxytolu-3:6-quinone, m.p. 200—204° (decomp.) (*loc. cit.*, 186°). With Br-CHCl_3 (IV) gives the 5-Br-derivative, m.p. 142°, from which alkalis do not remove Br smoothly and which with amines gives cryst. products containing Br. 1:2:4:5- $\text{C}_6\text{H}_2\text{Me}(\text{OMe})_3$ and Br-CHCl_3 give 3:6-dibromo-2:4:5-trimethoxytoluene, m.p. 75—77°, converted by HNO_3 (d 1.4) at 50° into 2:5-dibromo-4-methoxytoluquinone, m.p. 120—121°, from which the Br cannot be smoothly removed.

R. S. C.

Phenylethyl mercaptans. B. HOLMBERG (Arkiv Kemi, Min., Geol., 1937, 12, A, No. 14, 10 pp.).— $\text{CHPhMe}\cdot\text{OH}$, $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and HCl give α -phenylethylthiolacetic acid, m.p. 61—63°, converted by $\text{K}_2\text{S}_2\text{O}_8$ or H_2O_2 into α -phenylethylsulphoxidoacetic acid, $\text{CHPhMe}\cdot\text{SO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I), m.p. 117—119°, distillation of which in steam from dil. H_2SO_4 gives α -phenylethyl mercaptan, b.p. 87—88°/15 mm., and $\text{CHO}\cdot\text{CO}_2\text{H}$. With MgSO_4 this gives the Hg^{++} salt, m.p. 71—72°, and with HgCl_2 in EtOH the HgCl -derivative, m.p. 73—75°. In HCl , however, HgCl_2 gives $\text{HgCl}_2\cdot 2\text{HgS}$, $\text{CHPhMe}\cdot\text{OH}$, $\text{CHPh}\cdot\text{CH}_2$, CHPhMeCl , and $(\text{CHPhMe})_2\text{O}$, also obtained by distilling (I), HgCl_2 , and HCl in steam. $\text{CHPhMe}\cdot\text{OH}$ and N-HCl at 100° give some CHPhMeCl and $\text{CHPh}\cdot\text{CH}_2$. The HgCl -derivative, m.p. 213—232°, of β -phenylethyl mercaptan, b.p. 94—95°/13 mm. (Hg^{++} salt, m.p. 95—96°), is more stable, as it is obtained with $\text{CHO}\cdot\text{CO}_2\text{H}$ by distilling $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{SO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ with HgCl_2 and HCl in steam; the mercaptan is obtained by distilling the acid from dil. H_2SO_4 in steam.

R. S. C.

Aminoarylsulphones.—See B., 1938, 353.

Action of potassium hydroxide on α -chloro- β -phenylpropan- β -ol. A. M. CHALETZKI (J. Gen. Chem. Russ., 1937, 7, 2857—2860).— $\text{OH}\cdot\text{CPhMe}\cdot\text{CH}_2\text{Cl}$ and 20% KOH in aq. EtOH (4 hr at 100°) yield α -ethoxy- β -phenylpropan- β -ol (I), b.p. 127—128°/14 mm., together with $\text{CPhMe}\text{CH}_2\text{CH}_2\text{O}$. (I), when distilled from $\text{H}_2\text{C}_2\text{O}_4$ at 185°, gives β -phenylallyl *Et ether*, b.p. 86—

87°/18 mm., from which $\text{CHPhMe}\cdot\text{CHO}$ is obtained by heating with 20% H_2SO_4 (2 hr. at 100°). R. T.

Natural and synthetic ephedrine. B. BLEYER (Arch. Pharm., 1938, 276, 164—170).—A summary of the m.p. and $[\alpha]$ of natural and synthetic ephedrine (and salts), emphasising the identity of both materials.

J. D. R.

Phenanthrene derivatives. IX. 1-Hydroxy-1-alkyltetrahydrophenanthrenes and related compounds. W. E. BACHMANN and A. L. WILDS (J. Amer. Chem. Soc., 1938, 60, 624—627; cf. A., 1938, II, 90).—1-Keto-1:2:3:4-tetrahydrophenanthrene and MgMeI give 1-hydroxy-1-methyl-1:2:3:4-tetrahydrophenanthrene (84—88%), m.p. 86—86.5°, which, when heated at 180—200° and then sublimed, gives 1-methyl-(3:4)-dihydrophenanthrene (80%), m.p. 86—86.5°, converted by 30% Pd-C at 310—320° in 90% yield into 1-methylphenanthrene. Similarly are obtained 1-hydroxy-1-ethyl-, m.p. 57—57.5°, -*n*-propyl- (I), m.p. 87—87.5°, -isopropyl-, an oil, -*n*-butyl- (II), an oil, and -phenyl-1:2:3:4-tetrahydrophenanthrene, m.p. 115—115.5°, 1-ethyl-, m.p. 42—43°, -isopropyl-, m.p. 66—67°, and -phenyl-3:4-dihydrophenanthrene, m.p. 98°, 1-ethyl-, new m.p. 63.5—64° (picrate, m.p. 109.5—110°), 1-isopropyl-, new m.p. 88—88.5°, and 1-phenyl-phenanthrene, m.p. 79—79.5° (picrate, m.p. 117—117.5°). (I) and (II) are converted by Pd-C directly into 1-*n*-propyl- and 1-*n*-butyl-phenanthrene, m.p. 42° (picrate, m.p. 99—99.5°), respectively; the former product is, however, best obtained from 1-hydroxy-1-allyl-1:2:3:4-tetrahydrophenanthrene by Pd-C at 215—220°. Dehydration of the OH-compounds by KHSO_4 at 160° gives only some alkylphenanthrene, indicating disproportionation; by thus treating (II) and then dehydrogenating the product with S at 260° a 56% yield is obtained. MgMeI and 5-keto-5:6:7:8-tetrahydro-1:2-benzanthracene give 86% of 5-hydroxy-5-methyl-5:6:7:8-tetrahydro-1:2-benzanthracene, m.p. 91—95°, converted at 200—250° into 5-methyl-7:8-dihydro-1:2-benzanthracene (87%), m.p. 118—118.5°, and thence by Pd-C in 88% yield or less well by S into 5-methyl-1:2-benzanthracene; the Pd-C does not lose activity in the process. R. S. C.

Stereoisomerism of cyclohexane-1:3- and -1:4-diols. Preparation of the 1:3- and 1:4-diols. J. COOPS, J. W. DIENSK, and A. ATEN (Rec. trav. chim., 1938, 57, 303—315).—Resorcinol with $\text{H}_2\text{-Ni}$ in EtOH at 130—140°/70—80 atm. gives *cis*-cyclohexane-1:3-diol, m.p. 86°, and the *trans*-isomeride, m.p. 117°, purified through their $(\text{CPh}_3)_2$ ethers; the *cis*-ether, new m.p. 178°, is often obtained solvated (cf. Lindemann and Baumann, A., 1930, 209). Similarly quinol gives *cis*- (I), m.p. 112°, and *trans*- (II), m.p. 143°, -cyclohexane-1:4-diols. Some cyclohexanol is produced in both reductions. M.p. curves of (I) and (II), their respective $(\text{CPh}_3)_2$ ethers (m.p. 234° and 252°) and diacetates (m.p. 39° and 104°) indicate that the product described by von Baeyer (A., 1894, i, 174) as pure (I) is a mixture of 84% of (I) and 16% of (II); similarly the recorded diacetate of (I) contains 17% of the diacetate of (II). A. T. P.

Dealkylation of monoethers of C_5 and C_6 cyclane-1:2-diols by sulphuric acid. M. Mous-

SERON and R. GRANGER (Compt. rend., 1938, 206, 922—924; cf. A., 1937, II, 496).—ROH is eliminated from mono-ethers of *cyclopentane*- (I) and -*hexane* (II) -1 : 2-diols by hot H_2SO_4 . The Me and Et ethers of (I) yield *cyclopentadiene*. The ease of formation of *cyclopentanealdehyde* from Me (III), Et, Pr^a, and *cyclohexyl* ethers of (II) decreases in the order given; (III) also gives a little *methoxycyclohexene* whilst the Pr^a ether yields mainly *cyclohexadiene*. 2-Methoxy-1-methyl- and -1-ethyl-*cyclohexanol* give 2-methyl- and -ethyl-*cyclohexanone* and some *cyclopentyl* Me and Et ketone, respectively. *cyclohexanealdehyde* is obtained from 1-methoxycyclohexylcarbinol. A mechanism of the elimination of ROH, through a sulphuric ester [isolated from (III) at -10°] and a rearrangement from a C_6 to a C_5 structure, is discussed.

A. T. P.

Compounds of certain dyes of the triphenylmethane group with metallic salts. III. E. GHELLER (Ann. Sci. Univ. Jassy, 1938, 24, 196—200).—Treatment of a solution of the requisite dye with $\text{K}_3\text{Co}(\text{NO}_2)_6$ gives the salts $\text{R}'_3\text{Co}(\text{NO}_2)_6$, $\text{R}''_3\text{Co}(\text{NO}_2)_6$, and $\text{R}'''_3\text{Co}(\text{NO}_2)_6$ (where R', R'', and R''' are the org. residue of crystal-violet, malachite-green, and rhodamine B, respectively); the change does not appear to be exactly a double decomp. of ionic character. R'Cl is converted by a large excess of a very conc. solution of CdCl_2 into the salt, $2\text{R}'\text{Cl}, \text{CdCl}_2$, and by a large excess of conc. AgNO_3 into the substance, $\text{R}'\text{Cl}, 2\text{AgNO}_3$. The compounds, $2\text{R}''\text{Cl}, \text{CdCl}_2$ and $\text{R}'''\text{Cl}, 2\text{AgNO}_3$, are derived similarly. When the mother-liquors from the prep. of the maroon-violet $2\text{R}'\text{I}, \text{CdI}_2$ are boiled a green-violet salt of the same composition is pptd. Either product is transformed by conc. AgNO_3 into the same compound, $\text{R}'\text{NO}_3, 2\text{AgI}$, which with KI yields the substance, $\text{R}'\text{I}, 2\text{AgI}$. When the products are treated with hot $\text{K}_2\text{Fe}(\text{CN})_6$, two compounds (?), $\text{R}'_3(\text{FeC}_6\text{N}_6)_2, \text{Cd}_3(\text{FeC}_6\text{N}_6)_2$, differing from one another in colour are produced; with AgNO_3 these give the same substance, $\text{R}'\text{NO}_3, 2\text{AgI}$. The isomerism of these products is not established. $\text{R}'_3\text{Fe}(\text{CN})_6$ and conc. aq. AgNO_3 give the salt $\text{R}'_3\text{Fe}(\text{CN})_6, 4\text{AgNO}_3$.

H. W.

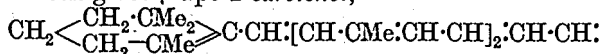
Stereoisomerism of steroids. J. W. DIENSKE (Chem. Weekblad, 1938, 35, 243—250).—A review of the stereochemistry of the more important sterols.

S. C.

Alcohols of the ætiocholane series.—See B., 1938, 457.

Hydrogenation of cestrin and its œstrogenous derivatives.—See B., 1938, 457.

Homologue of vitamin-A (axerophthol) and a degradation product of α -carotene, α -apo-2-carotenol. H. VON EULER, P. KARRER, and U. SOLMSEN (Helv. Chim. Acta, 1938, 21, 211—222).—Reduction of β -apo-2-carotenol (I) with $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH gives β -apo-2-carotenol,

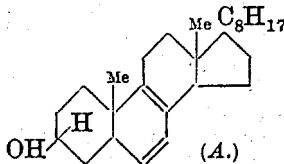


$\text{CMe} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CMe} \cdot \text{CH}_2 \cdot \text{OH}$, m.p. 145° (sinters at 143°), which is not identical with the chromogen of the livers of fresh- H_2O fish. Partial oxidation of β -carotene (II) by KMnO_4 yields

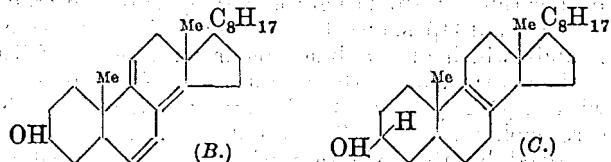
(I) as main product, followed by β -apo-4-carotenol. Occasionally the production of β -apo-3-carotenol is observed in amount too small to permit complete purification. Chromatographic analysis of the crude product (Al_2O_3) shows the presence of several compounds which give a blue colour with SbCl_3 whilst similar treatment of the product left after reduction with $\text{Al}(\text{OPr}^i)_3$ points to the production of β -apo-5-carotenol, m.p. 42° . The product, m.p. 169 — 170° , obtained by the oxidation of (II) and regarded as ψ - α -carotene is shown to be α -carotene, m.p. 182° , probably present as impurity in the original material. Analogous oxidation of α -carotene yields mainly α -apo-2-carotenol (III), m.p. 158° , $[\alpha]_{\text{D}}^{25} + 365^\circ \pm 20^\circ$, $[\alpha]_{\text{D}}^{626} + 538^\circ \pm 25^\circ$, $[\alpha]_{\text{D}}^{644} + 692^\circ \pm 35^\circ$, $[\alpha]_{\text{D}}^{644} + 461^\circ \pm 25^\circ$, $[\alpha]_{\text{D}}^{608} + 615^\circ \pm 30^\circ$ in C_6H_6 (oxime, m.p. 178°). In an individual experiment partial oxidation of an unpurified carotene from beet gave an α -apo-2-carotenol, m.p. 174° (oxime, m.p. 185°), which is not isomerised to (III) by I. Reduction $[\text{Al}(\text{OPr}^i)_3]$ of (III) affords α -apo-2-carotenol, m.p. 157° after softening at 150° . The above cited β -compounds show strong vitamin-A activity whereas the α -derivatives are inactive.

H. W.

isoDehydrocholesterol [$\Delta^{6,8}$ -cholestadien-3-ol]. A. WINDAUS, O. LINSERT, and H. J. ECKHARDT (Annalen, 1938, 534, 22—41).—The isolation of iso-dehydrocholesterol (I), m.p. 120 — 122° , $[\alpha]_{\text{D}}^{25} - 17.9^\circ$ in CHCl_3 , with 7-dehydrocholesterol (II) from the products of the thermal decomp. of 7-hydroxycholesterol dibenzoate (cf. A., 1935, 1363) is described. (I) gives an acetate (III), m.p. 111 — 112° , becoming transparent at 118 — 120° , $[\alpha]_{\text{D}}^{25} - 10.7^\circ$ in CHCl_3 , a benzoate, m.p. 146° , becoming transparent at 180° , a 3 : 5-dinitrobenzoate, m.p. 200 — 202° (decomp.), $[\alpha]_{\text{D}}^{25} - 2.6^\circ$ in CHCl_3 , and a p-nitrobenzoate, m.p. 165° (cloudy), $[\alpha]_{\text{D}}^{25} - 6.5^\circ$ in CHCl_3 . Its ultra-violet absorption spectrum resembles closely that of (II) and establishes the presence of conjugated linkings probably contained in the same ring. Maleic anhydride and (I) in xylene at 135° yield (after treatment with 15% $\text{EtOH}-\text{NaOEt}$) cholestadienol C, m.p. 110° , $[\alpha]_{\text{D}}^{25} - 2.7^\circ$ in CHCl_3 (acetate, m.p. 99°), which according to its spectrum contains a system of conjugated linkings distributed over two rings, and isodehydrocholesterol-maleic acid, m.p. 228° (Me_2 ester, m.p. 89°), converted by Ac_2O at 100° into α -isodehydrocholesteryl acetate-maleic anhydride, m.p. 196° after softening at 180° , $[\alpha]_{\text{D}}^{25} - 79.5^\circ$ in CHCl_3 , which when distilled in a vac. becomes isomerised to β -isodehydrocholesteryl acetate-maleic anhydride, m.p. 201° . Oxidation of (III) with HNO_3 (d 1.4) gives 1 : 2 : 3 : 4 : 5- $\text{C}_6\text{HMe}(\text{CO}_2\text{H})_4$. Exposure of (II) in EtOH to sunlight in presence of eosin and absence of air gives a bimol. product, $\text{C}_{54}\text{H}_{86}\text{O}_2$, m.p. 195 — 196° (diacetate, m.p. 202° , $[\alpha]_{\text{D}}^{25} - 134^\circ$ in CHCl_3 ; dipropionate, m.p. 197°), apparently identical with the products obtained similarly from (II) and, like them, converted by Ac_2O into CH_4 and the norsterol, $\text{C}_{26}\text{H}_{40}\text{O}$. The possibility that (I) and (II) differ sterically is disproved since the same products (α -cholesterol and



cholestanol) are obtained by the catalytic hydrogenation of each. (I) is therefore (A). BzO_2H smoothly transforms (III) into 9-hydroxycholestadienyl acetate,



m.p. 138° , $[\alpha]_D^{25} -17.8^\circ$ in CHCl_3 , which contains a *tert.*-OH since it evolves CH_4 with MgMeI but is not acetylated by $\text{C}_5\text{H}_5\text{N}-\text{Ac}_2\text{O}$ at 100° ; it is hydrolysed to the very unstable 9-hydroxycholestadienol, m.p. 143° , $[\alpha]_D^{25} -19.7^\circ$ in CHCl_3 , and converted by boiling Ac_2O followed by distillation in a vac. into cholestatrienol (B), m.p. 159° , $[\alpha]_D^{25} -99^\circ$ in CHCl_3 (acetate, m.p. 148°). Reduction of (I) with Na and Pr^nOH gives 8-cholestenol [probably (C)], m.p. $120-121^\circ$, $[\alpha]_D^{25} +12.2^\circ$ in CHCl_3 [acetate (IV), m.p. 108° , $[\alpha]_D^{25} +13.8^\circ$ in CHCl_3 ; benzoate, m.p. 147° , becoming transparent at 174°], with minor amounts of ϵ -cholestenol (acetate, m.p. 118° , $[\alpha]_D^{25} +20.9^\circ$). (IV) is isomerised by H_2 -Pd-EtOAc to α -cholestenyl acetate. BzO_2H converts (IV) into (?) Δ^7 -cholestene-3:9-diol, the acetate, m.p. $102-103^\circ$, of which is transformed by Ac_2O at 100° into cholestadienyl (D) acetate, m.p. $98-99^\circ$. HCl converts (I) into the cholestadienol B_3 derived previously (A., 1937, II, 59) from (II); its acetate and maleic anhydride in boiling C_6H_6 give an adduct, m.p. $202-203^\circ$, $[\alpha]_D^{25} -58.4^\circ$ in CHCl_3 .

H. W.

epiErgosterol. A. WINDAUS and K. BUCHHOLZ (Ber., 1938, 71, [B], 576-578).—The compound obtained by Marker *et al.* (A., 1937, II, 496) is not *epi*ergosterol since its absorption spectrum differs greatly from that of ergosterol. It is probably $\Delta^4:7:22$ -ergostatrien-3-ol (acetate, m.p. $126-127^\circ$, $[\alpha]_D^{25} +92.5^\circ$ in CHCl_3 ; 3:5-dinitrobenzoate, m.p. $164-165^\circ$).

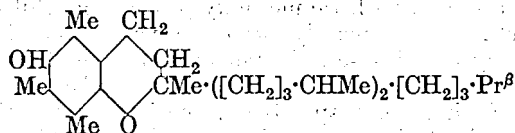
H. W.

Sex hormones. XXIX. Preparation of 17-ethynyltestosterone and of Δ^5 -3-trans-17-dihydroxy-17-vinylandrosterone. L. RUZICKA, K. HOFMANN, and H. F. MELDAHL (Helv. Chim. Acta, 1938, 21, 371-374).— Δ^5 -17-Acetylenylandrosterone-3-trans-17-diol (I) (A., 1937, II, 505) in anhyd. COMe_2 is converted by $\text{Al}(\text{O}i\text{Bu})_3$ in boiling C_6H_6 into 17-acetylenyltestosterone (II), m.p. $270-272^\circ$, $[\alpha]_D^{25} +22.5^\circ$ in dioxan [oxime, m.p. $234-235^\circ$ (decomp.)]. Partial hydrogenation (Ni in EtOH at room temp.) of (I) gives Δ^5 -17-vinylandrosterone-3-trans-17-diol, m.p. $183-184^\circ$, $[\alpha]_D^{25} -84^\circ$ in dioxan, transformed by $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ at room temp. into the 3-acetate, m.p. $160-161^\circ$. The physiological action of (II) resembles that of progesterone. All m.p. are corr.

H. W.

Constitution of α -tocopherol. E. FERNHOLZ (J. Amer. Chem. Soc., 1938, 60, 700-705).—Duroquinol sec.-Bu, m.p. $85-86^\circ$, dodecyl, m.p. $93-94^\circ$, cetyl, m.p. 101° , octadecyl, m.p. 105° , β -methyl-n-octadecyl, m.p. $94-95^\circ$, and n-nonadecyl (? α -methyl-n-octadecyl) ether, m.p. $94-95^\circ$, differ from α -tocopherol (I) in having an absorption max. at $2900-3000 \text{ \AA}$. with $\epsilon_{\text{max}}^{1\%} 73$ and in being oxidised to duroquinone (II) by AgNO_3 . With AgNO_3 (I) gives an oil of about the

same mol. wt. and it is unaffected by HI (cf. John, A., 1937, III, 497). With AlCl_3 (I) gives traces of (II). At 355° (I) gives a combustible gas, duroquinol, and a mono-unsaturated (Br; not to BzO_2H) hydrocarbon, (?) $\text{C}_{18}\text{H}_{36}$. Thus, (I) is not a simple duroquinol ether and the aliphatic side-chain must be connected to the Ph by a C-C linking. The annexed formula is



propounded and is supported by the results of oxidation. With CrO_3 in aq. AcOH at room temp. (I) gives $(\text{CMe}\cdot\text{CO})_2\text{O}$ and a lactone (III),

$\text{C}_{16}\text{H}_{33}\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}$, an oil; the corresponding acid (IV) (benzylthiuronium salt, m.p. 120° , $[\alpha]_D^{25} +4.6^\circ$ in dry EtOH) readily lactonises. The Me ester, b.p. $140/0.02 \text{ mm.}$, of (IV), prepared from (III) by $\text{H}_2\text{SO}_4\text{-MeOH}$, is partly oxidised by CrO_3 ; the OH could not be esterified and is thus *tert.* With an excess of CrO_3 in hot aq. AcOH α -tocopheryl acetate gives Ac_2 [di-p-nitrophenylosazone, m.p. 330° (decomp.)], COMe_2 , a ketone, $\text{C}_{18}\text{H}_{36}\text{O}$ (reduced by Na-EtOH to an alcohol, giving a 3:5-dinitrobenzoate, m.p. $101-103^\circ$), and an acid, $\text{C}_{16}\text{H}_{32}\text{O}_2$, b.p. 150° (bath temp.)/0.02 mm. (benzylthiuronium salt, m.p. 146°), which by the isoprene rule and from the fact that its p-phenylphenacyl ester, m.p. 49° , $[\alpha]_D^{25} -8.7^\circ$ in CHCl_3 , gives (Kuhn) 2 AcOH is probably $\gamma\gamma$ -trimethyltridecoic acid.

R. S. C.

Inositolphosphoric acid compounds. IV. Bis-muth inositolphosphate. V. Copper and copper ethylenediamine inositolphosphates. VI. Manganese inositolphosphate. S. OTOLSKI (Arch. Chem. Farm., 1937, 3, 231-234, 255-257, 258-259).—IV. The Bi_4 salt of inositolphosphoric acid is described.

V. The product obtained when $\text{Cu}(\text{OAc})_2$ is added to MgCa inositolphosphate in 5% AcOH is $\text{C}_6\text{H}_{10}\text{O}_{24}\text{P}_6\text{Cu}_4$ (I), and not $\text{C}_6\text{H}_6\text{O}_{24}\text{P}_6\text{Cu}_6\cdot 3\text{H}_2\text{O}$, as stated by Anderson (A., 1912, i, 676). (I) gives a sol. additive compound, $\text{C}_6\text{H}_{10}\text{O}_{24}\text{P}_6\text{Cu}_4\cdot 6(\text{CH}_2\cdot\text{NH}_2)_2$, with $(\text{CH}_2\cdot\text{NH}_2)_2$.

VI. MnSO_4 and aq. inositolphosphoric acid yield the insol. salt $\text{C}_6\text{H}_6\text{O}_{24}\text{P}_6\text{Mn}_6$.

R. T.

Isolation and properties of gorlic [μ - Δ^2 -cyclopentenyl- Δ^4 -tridecenoic] acid, an optically active liquid fatty acid. H. I. COLE and H. T. CARDOSO (J. Amer. Chem. Soc., 1938, 60, 612-614).—The acids from *Carpotroche brasiliensis* or *Oncoba echinata* are freed as far as possible from solid acids in cold 80% EtOH. The liquid constituents, 25.2 and 20.8%, respectively, decompose greatly when distilled, but fractionation (Podbielniak) of the Et esters involves only a 2.4% loss. Thus are obtained oleic and gorlic acid, m.p. 6° , b.p. 232.5° (decomp.)/10 mm., $[\alpha]_D^{25} +60.7^\circ$ in CHCl_3 (Me, b.p. $209/10 \text{ mm.}$, m.p. $<10^\circ$, $[\alpha]_D^{25} +57.7^\circ$ in CHCl_3 , and Et ester, b.p. $214/10 \text{ mm.}$, m.p. $<10^\circ$, $[\alpha]_D^{25} +55.4^\circ$ in CHCl_3).

R. S. C.

Chaulmoogric acid series. I. New synthesis of dihydrohydnicarpic acid. K. V. BOKIL and

K. S. NARGUND (J. Univ. Bombay, 1937, 6, Part II, 93—96).—The K derivative of Et cyclopentanone-2-carboxylate and Et κ -bromoundecate give the di-ester (75%), hydrolysed and decarboxylated (conc. HCl) to κ -2-ketocyclopentylundecic acid, b.p. 240—260°/9 mm. (semicarbazone, m.p. 162—163°), which is reduced (Clemmensen) to dihydrohydno-carpic acid.

F. R. S.

Aliphatic-acylated triarylmethane dyes. T. WAGNER-JAUREGG and K. REINEMUND (J. pr. Chem., 1938, [ii], 150, 250—256).—Chaulmoogryl chloride (I), b.p. 150—160°/0.2 mm., and fuchsin in C_5H_5N give only *dichaulmoogrylfuchsin* (unstable hydrochloride), insol. in H_2O and dil. acid. The *dichaulmoogryl* derivative of "Neufuchsin" is similarly prepared. α - $C_{10}H_7$. NH_2 and (*p*- NMe_2 . C_6H_4) $_2$ CH.OH are condensed by HCl-EtOH, purified by $SnCl_2$ and H_2S , oxidised by chloranil to the dye, and then condensed with undecenyl chloride and K_2CO_3 in hot C_6H_6 to the green dye, 1:4- CH_2 :CH[CH_2] $_8$.CO.NH. $C_{10}H_6$.C(C_6H_4 . NMe_2 .OH-*p*). C_6H_4 . NMe_2 -*p*. An anhydride, m.p. 53—55°, is often obtained when impure (I) is kept at about 0°.

R. S. C.

Polymethylbenzenes. XX. Addition of ethyl diazoacetate to prehnitene. L. I. SMITH and C. L. AGRE (J. Amer. Chem. Soc., 1938, 60, 648—652; cf. A., 1937, II, 372).—XX. Addition of CHN_2 .CO $_2$ Et to prehnitene at 140° gives rapidly N_2 and esters, b.p. 123—129°/3.5 mm. and 131—138°/3.5 mm., respectively, hydrolysed to 3:4:5:6-tetramethyl- $\Delta^{1:3:6}$ -cycloheptatrienecarboxylic acid, m.p. 168—170° (170—173°) [unsaturated, yellow colour in H_2SO_4 ; other oily acids (A) of similar structure are also obtained], and β -2:3:4-trimethylphenylpropionic acid (I), m.p. 143°, respectively. Heating for only a short time at 140° gives a liquid, which may be a norcaradiene derivative, since it gives a red colour with H_2SO_4 . Other modifications, e.g., reaction at a lower temp., did not lead to indazolines or definite norcaradiene derivatives. With HBr-AcOH at room temp. (A) gives 2:3:4:5- C_6HMe_4 .CH $_2$.CO $_2$ H (II), new m.p. 159—161°. Addition of 1:2:3:4- $C_6H_2Me_3$ Br and EtBr and then of $(CH_2)_2O$ to Mg in Et_2O gives impure β -2:3:4-trimethylphenylethyl alcohol, b.p. 142—145°/9 mm. (3:5-dinitrobenzoate, m.p. 164—165°; phenylurethane, m.p. 127—128°), converted by HBr-AcOH at 100° into the bromide, b.p. 138—141°/10 mm., which with NaCN in aq. EtOH gives β -2:3:4-trimethylphenylpropionitrile, b.p. 159—163°/13 mm., m.p. 63°, and thence by 1:1 aq. H_2SO_4 at 100° (I). 1:2:3- $C_6H_3Me_3$.HCl, $Zn(CN)_2$, and $AlCl_3$ in C_6H_6 at 50° give 2:3:4-trimethylbenzaldehyde (III), b.p. 121.5°/11 mm., m.p. 7—8° (oxime, m.p. 131—132°), and thence by standard methods Et_2 2:3:4-trimethylbenzylidenemalonate, m.p. 76—77°, the corresponding acid, m.p. 196—197°, 2:3:4-trimethylbenzylmalonic acid, m.p. 175—176° (decomp.), and thence (I). CH_2 (CO $_2$ H) $_2$ (III), and a little piperidine give 2:3:4-trimethylcinnamic acid, m.p. 207—208°, reduced by Na-Hg in Na_2CO_3 to (I). Prehnitene, HCl, $Zn(CN)_2$, and $AlCl_3$ in C_6H_6 afford 2:3:4:5-tetramethylbenzaldehyde, m.p. 29—30°, b.p. 142—144°/15 mm. (oxime,

m.p. 152.5—153.5°; semicarbazone, m.p. 221—222°; very sensitive to O_2), reduced by Zn dust in aq. AcOH to 2:3:4:5-tetramethylbenzyl alcohol, m.p. 80—81°, which with HCl yields the chloride, m.p. 44—45°, b.p. 139—140°/15 mm., and thence 2:3:4:5-tetramethylphenylacetoneitrile, m.p. 57—58°, and (II).

R. S. C.

(+)-Phenylchloroacetoneitrile and related compounds. I. A. SMITH (Ber., 1938, 71, [B], 634—643).— $SOCl_2$ and (—)-OH.CHPh.CO.NH $_2$ at room temp. afford (—)-phenylchloroacetamide (I), m.p. 138—139°, [α] $^{20}_{D}$ —94.1°, [α] $^{20}_{D_{41}}$ —99.1°, [α] $^{20}_{D_{61}}$ —115.0° in $COMe_2$, [α] $^{20}_{D_{41}}$ —119.7° in MeOH. It is very rapidly catalytically racemised by KOH-MeOH. Comparison with *p*- C_6H_4 Me.CHPh.CO.NH $_2$ and OH.CHPh.CO.NH $_2$ shows that Cl and *p*- C_6H_4 Me have much greater enolising power than OH. Dehydration of (I) with P_2O_5 in PhMe affords (+)-phenylchloroacetoneitrile (II), b.p. 117—118°/18 mm., m.p. 24—25°, [α] $^{20}_{D}$ +44.8°, [α] $^{20}_{D_{41}}$ +50.2° in $COMe_2$, [α] $^{20}_{D_{41}}$ +46.5° in EtOH, converted by prolonged boiling with conc. HCl into *r*-CHPhCl.CO $_2$ H. (II) is immediately racemised by KOH-EtOH, more slowly by EtOH; MeOH, dried over CaO and distilled over Ca, causes immediate racemisation whereas the technical alcohol is much less active due to traces of acid. (II) is much more easily racemised than OH.CHPh.CN or OMe.CHPh.CN. *r*-CHPhCl.CO.NH $_2$ is converted by Cu-bronze in PhMe at 140° into diphenylsuccinamide, m.p. 220°. *r*-CHPhBr.CO $_2$ H and Cu-bronze at 100° give mesodiphenylsuccinic acid, m.p. 242—243°, also obtained from mol. Ag or Cu-bronze and *r*-CHPhCl.CO $_2$ H. *r*-CHPhCl.CN is transformed by MgPhBr into phenyldeoxybenzoin (III) and a compound, m.p. 216—217°, which contains N and Cl. (III) is also derived similarly from *r*-CHPhCl.CO.NH $_2$. CHPh $_2$.CN, from CHPh $_2$.CO.NH $_2$ and P_2O_5 in PhMe, is transformed by MgPhBr into (III) and tetraphenylsuccinodinitrile, m.p. 204—205°.

H. W.

Orientation phenomena of phenolic derivatives in their reaction with the phenylglycollic acids.

II. Condensation of mandelic acids with cresols, xyenols, and other substituted phenols. III. Condensation of mandelic acid with *m*-hydroxybenzoic acids. IV. Oxidation of *o*-hydroxydiphenylacetolactones by calcium permanganate. B. I. ARVENTI (Ann. Sci. Univ. Jassy, 1938, 24, 72—86, 103—109, 219—231).—II. PhOH and OH.CHPh.CO $_2$ H in a sealed tube without condensing agent at 230—235° give *o*-hydroxydiphenylacetolactone (I), m.p. 114° (yield 53%), and *p*-hydroxydiphenylacetic acid, m.p. 173°. A similar result is obtained when the reactants are boiled together. Under like conditions *p*-cresol gives 2-hydroxy-5-methyldiphenylacetolactone (II), m.p. 106°, in 68% yield. Similarly *o*-cresol gives 2-hydroxy-3-methyldiphenylacetolactone (III), m.p. 65° [whence 2-hydroxy-3-methyldiphenylacetic acid, m.p. 84—85° (Ag and Cu salts), which slowly lactonises at room temp.], and 4-hydroxy-3-methyldiphenylacetic acid, m.p. 136—137°. *m*-Cresol gives 2-hydroxy-4-methyldiphenylacetolactone (IV) in 38% yield [whence 2-hydroxy-4-methyldiphenylacetic acid, m.p. 52° (Ag and Cu salts)], and 2-hydroxy-6-methyldiphenylacetolactone, m.p. 77°.

in 11% yield. *o*-4-Xylenol gives 2-hydroxy-4:5-dimethyldiphenylacetolactone (V), m.p. 93° [corresponding acid, m.p. 74° (*Na* salt)], and 2-hydroxy-5:6-dimethyldiphenylacetolactone, m.p. 100° (yield 15%). *m*-5-Xylenol yields 2-hydroxy-4:6-dimethyldiphenylacetolactone, m.p. 112°, in 65–73% yield; the corresponding acid is so readily lactonised that it cannot be obtained pure. 2-Hydroxy-3:5-dimethyldiphenylacetolactone (III), m.p. 70°, is produced in 63% yield from *m*-4-xylenol; the corresponding acid is non-cryst. and unstable. *p*-Xylenol gives 2-hydroxy-3:6-dimethyldiphenylacetolactone, m.p. 101–102°, in 52% yield. Thymol affords 2-hydroxy-6-methyl-3-isopropylidiphenylacetolactone, m.p. 105–106° (yield 47%); the corresponding acid is lactonised immediately after acidification of its *Na* salt. 2-Hydroxy-3-methyl-6-isopropyl-, m.p. 77–78°, and 2-hydroxy-3-ethyl-, m.p. 85–86°, -diphenylacetolactone are obtained from carvacrol and *o*-C₆H₄Et·OH, respectively.

III. Condensation between OH·CHPh·CO₂H and phenols with CO₂H in *meta* position to OH occurs exclusively with replacement of H between OH and CO₂H and production of the corresponding lactone which is cyclised to an anthranol lactone. *m*-OH·C₆H₄·CO₂H and OH·CHPh·CO₂H at 230–250° give 2-hydroxy-6-carboxydiphenylacetolactone CO₂H·C₆H₄·CHPh, m.p. 242–244°, transformed by

boiling Ac₂O into the Ac derivative, m.p. 221°, of 1-hydroxyanthranol-9-carboxylactone, whence the free lactone, m.p. 280° (decomp.), oxidised by H₂O₂ and Na₂CO₃ to (?) erythrohydroxyanthraquinone, m.p. 191–193°. Similarly 2:1:4-OH·C₆H₃Me·CO₂H and OH·CHPh·CO₂H yield 2-hydroxy-6-carboxy-3-methyldiphenylacetolactone, m.p. 275–280° (decomp.), whence 1-hydroxy-2-methylantranol-9-carboxylactone, m.p. 292°, and its Ac derivative, m.p. 233°.

IV. *o*-Hydroxydiphenylacetic acids with Me at C₍₆₎ are unstable and are immediately transformed into the corresponding lactones, thus permitting the elucidation of the structure of isomeric lactones. Lactones without a substituent at C₍₆₎ are oxidised by Ca(MnO₄)₂ to the corresponding dilactones whereas under these conditions lactones methylated at C₍₆₎ give resinous products with occasional traces of peroxides of dilactones. Oxidation of (I) by Ca(MnO₄)₂ in COMe₂ yields 2:2'-dihydroxytetraphenylsuccinodilactone, m.p. 177°. Similarly (II) affords the corresponding dilactone, m.p. 195–197°, in 56% yield but a different product appears to result if KMnO₄ is used. The dilactone, m.p. 187°, is formed from (IV) and Ca(MnO₄)₂. (III) and 4-chloro-2-hydroxydiphenylacetolactone give respectively 2:2'-dihydroxy-3:3'-dimethyl-, m.p. 203° (80% yield), and 5:5'-dichloro-2:2'-dihydroxy-tetraphenylsuccinodilactone, m.p. 191–193°. (VI) gives 2:2'-dihydroxy-3:5:3':5'-tetramethyltetraphenylsuccinodilactone, m.p. 200°. 2:2'-Dihydroxy-4:4':5:5'-tetramethyltetraphenylsuccinodilactone (+C₆H₆), m.p. 177–179°, is obtained by the oxidation of (V) or from the *Na* derivative of (V) and I in Et₂O. OH·CHPh·CO₂H and *p*-C₆H₄Bu⁺·OH at 245–250° afford 2-hydroxy-5-tert-butylidiphenylacetolactone, m.p. 136–137°, oxidised to 2:2'-dihydroxy-5:5'-ditert-butyltetraphenylsuccinodilactone, m.p. 202–203°. Similarly, 2-hydroxy-5-tert-

amylidiphenylacetolactone, b.p. 215–220°/10 mm., m.p. 58°, is oxidised to 2:2'-dihydroxy-5:5'-ditert-amyltetraphenylsuccinodilactone, m.p. 216°, and phenyl-1-hydroxy-2-naphthylacetolactone gives diphenyl-1:1'-dihydroxy-2:2'-dinaphthylsuccinodilactone (+1.5C₆H₆ or +1.5PhMe), m.p. 190–191°. The peroxide, m.p. 191–193° (violent decomp.), of 2:2'-dihydroxy-6:6'-dimethyl-3:3'-diisopropyltetraphenylsuccinodilactone is described.

The condensation of OH·CHPh·CO₂H with phenols can frequently be applied to elucidating the ease of substitution of the H atoms in the latter. In 8-hydroxyquinoline only H at C₍₅₎ (at C₍₄₎ with respect to OH) can be substituted. In α-C₁₀H₇·OH and *o*-cresol substitution occurs preferentially in position 2 with reference to OH and only to a small extent in position 4. With phenolic derivatives which have two differing *o*-positions the reaction is suitable for determining the relative ease of substitution of H in these positions: With *m*-cresol and *o*-xylenol the ratio of the lactones formed by substitution of the H atoms in positions 2 and 6 with respect to OH is about 3–3.5:1. H. W.

Condensation of methyl δ-phenyl-lævulate with sodium methoxide. S. ESKOLA (Suomen Kem., 1938, 11, B, 9–10).—Me δ-phenyl-lævulate and NaOMe give, after acidification, a substance, C₁₁H₁₀O₂, m.p. 233–234°, for which the structure CHPh<math display="block">\begin{array}{c} \text{CO}\cdot\text{CH}_2 \\ \text{CO}\cdot\text{CH}_2 \end{array} is assigned. F. R. S.

Phenylglutaric acids. II. β-Phenyl-β-methylglutaric acid. N. L. PHALNIKAR and K. S. NARGUND (J. Univ. Bombay, 1937, 6, Part II, 102–103).—COPhMe and CN·CH₂·CO₂Et in NH₃·EtOH give a cyano-imide, m.p. 270° (small yield), hydrolysed to β-phenyl-β-methylglutaric acid, m.p. 132–133° (*Ba*, *Ca*, and *Ag* salts). CPhMeCl₂ and CHNa(CO₂Et)₂ in C₆H₆ afford a condensation product, hydrolysed to the acid, in small yield. F. R. S.

Constitution and derivatives of α-phenylglutaconic acid. N. L. PHALNIKAR and K. S. NARGUND (J. Univ. Bombay, 1937, 6, Part II, 97–101).—α-Phenylglutaconic acid (I) (*Cu* and *Ag* salts) is oxidised (KMnO₄) to BzOH; with H₂O under pressure it gives styrylacetic acid, with boiling conc. HCl it forms a polymeride of CHPh·CHMe, and with aq. 25% KOH at 100° (sealed tube) it is recovered unchanged. The evidence is thus in favour of the *trans*-structure CO₂H·CH₂·CH·CPh·CO₂H. AcCl and (I) at 100° (sealed tube) give a mixture of 6-hydroxy-(II), m.p. 174–175°, and 6-chloro-, m.p. 110–111°, -3-phenyl-1:2-pyrone; with NH₂Ph at 150°, (I) affords a mixture of *trans*-semianilide, m.p. 96°, and dianilide, m.p. 90°. (II) and NH₂Ph in C₆H₆ give the *cis*-semianilide, m.p. 156°, of (I). F. R. S.

Criticism of the synthesis by Dixit of β-*p*-hydroxy-(or -*p*-methoxy-)phenylglutaconic acid from the corresponding glutaric acid. N. L. PHALNIKAR and K. S. NARGUND (J. Univ. Bombay, 1937, 6, Part II, 104–106).—Et β-*p*-anisylglutarate and PBr₅ give some 3- but no α-Br-derivative (cf. Dixit, A., 1932, 512) and a little β-*p*-anisylglutaric acid. F. R. S.

Isomeric diphenyldimethylsuccinic acids. A. MCKENZIE and A. RITCHIE (Ber., 1938, **71**, [B], 643—647).—*r*-CPhMeCl·CO₂H and MgEtBr in Et₂O yield *r*-*s*-diphenyldimethylsuccinic acid (α -form), m.p. 197—198° (decomp.) [anhydride (I), m.p. 159—160°]. (—)-CPhMeCl·CO₂H and MgPhBr give a dextro-rotatory acid which could not be isolated in an optically pure form. (I) is also obtained from Cu powder and *r*-CPhMeCl·CO₂H, which with mol. Ag yields meso-*s*-diphenyldimethylsuccinic acid (β -form), m.p. 197—199°. Na and *r*-CPhMeCl·CO₂H in Et₂O give atropic acid. The *s*-diphenyldimethylsuccinic acid of Schlenk and Bergmann (A., 1928, 1035) may be an *as*-derivative. H. W.

Catalytic hydrogenation using colloidal rhodium. C. ZENGHELIS and (MLLE.) C. STATHIS (Compt. rend., 1938, **206**, 682—683; cf. A., 1920, ii, 380).—CHPh·CH·CO₂H, maleic and fumaric acid with colloidal Rh—H₂ afford H₂-derivatives; PhCN gives (CH₂Ph)₂NH and small amounts of NH₃ and PhCHO; PhNO₂ yields NH₂Ph; COMe₂ affords Pr^oOH; (NPh)₂ gives NH₂Ph and then NH₃ and cyclohexane (I); C₆H₆ yields (I). These reactions occur almost quantitatively. Rh is much more active than Pt or Pd. J. L. D.

Polymorphism of crystalline-liquid arylidene-*p*-aminocinnamic esters; processes of association. D. VORLÄNDER [with R. WILKE, U. HABERLAND, K. THINIUS, H. HEMPEL, and J. FISCHER] (Ber., 1938, **71**, [B], 501—519; cf. A., 1938, I, 181).—The different cryst.-liquid forms of arylidene-*p*-aminocinnamic esters are closely similar to those of the *p*-azocinnamic esters (A., 1937, II, 493). Alterations in chemical structure at individual parts of the mol. hinder the development of the optimal trinity of cryst.-liquid phases, the *Pl* phases being mainly affected from the arylidene side and the *Rs* phases from the cinnamic side. More marked branching and angle formation can completely inhibit the formation of cryst.-liquid phases. When the stepwise appearance and disappearance of the different cryst.-liquid forms of one and the same substance is considered in conjunction with the definite, cryst. associatively favoured regions of union of the mol., it is obvious that the regions responsible for the cryst.-liquid arrangement are operative in the corresponding solid crystals. This is true even when the union relationships in the solid lattice are considerably more complex than in the cryst.-liquid lattice. The following are described: *Et* benzylidene-*p*-aminocinnamate, m.p. 64—66°, the corresponding *Me* ester, m.p. 131°, and acid, m.p. about 200° (decomp.); *Et* *p*-methylbenzylidene-*p*-aminocinnamate, amorphous liquid $\xrightleftharpoons{121^\circ}$ cryst. liquid I (*Bz* form) $\xrightleftharpoons{101^\circ}$ cryst. liquid II (*Rs* form) $\xrightleftharpoons{95^\circ}$ cryst. solid, and the corresponding *Me* ester, m.p. 151° (corr.), and acid, m.p. about 230° (incipient decomp.); *Et* *m*-, m.p. 74°, and *o*-, m.p. 61—63°, -methylbenzylidene-*p*-aminocinnamate; *Et* cinnamylidene-*p*-aminocinnamate, m.p. 101°, the corresponding *Me* ester, m.p. 164°, and acid, m.p. about 185° (much decomp.) after softening at 165°; *Et* *p*-phenylbenzylidene-*p*-aminocinnamate, transition temp. 145°, 180°, 208—209°, 212°, and 220°, and the *Me* ester, which becomes viscous and translucent at 208°, mobile and very cloudy at 220°, and transparent at 256°; *p*-phenylbenzylidene-*p*-aminodiphenyl, m.p. 243—245° to a cryst. liquid and m.p. 254° to an amorphous liquid; *Et* *p*-hydroxybenzylidene-*p*-aminocinnamate, m.p. 188—190°, its *Bz*, m.p. about 191° after softening at 129° to a translucent mass which becomes mobile at 198° and transparent at 223°, and *O*-CO₂*Et*-derivative, which softens at 90—92°, flows at about 119—120°, melts at 133° to a cloudy liquid which becomes transparent at 153°; *Et* anisylidene-*p*-aminocinnamate, the corresponding *Me* ester and acid, m.p. about 210°; *Et* *p*-ethoxybenzylidene-*p*-aminocinnamate, softens at 78—80°, passes into a viscous liquid at 112—114°, becomes mobile and translucent at 153°, and transparent at 159°, the corresponding *Me* ester, which becomes viscous at about 135°, mobile and translucent at 157—159°, and transparent at 194°, and acid, decomp. >215° after softening at 210°; *p*-ethoxybenzylidene-*p*-phenetidine, m.p. 148° (cryst. solid to amorphous liquid) or m.p. 143° (cryst. liquid to amorphous liquid); the condensation products, m.p. 120° and 123°, from *p*-NH₂·C₆H₄·CH:CH·CO₂Et and 2 : 1 : 5- and 3 : 1 : 6-OMe·C₆H₃Me·CHO, respectively; *Et* piperonylidene-*p*-aminocinnamate, m.p. 119—121°, and the *Me* ester, m.p. (capillary), 160—161°; *Et* *p*-nitrobenzylidene-aminocinnamate, m.p. 174—176°, and the corresponding *Me* ester, m.p. 215°, and acid, m.p. 240—245° (incipient decomp.); *p*-nitrobenzylidene-*p*-nitroaniline, m.p. 206°; *Et* *p*-dimethylaminobenzylidene-*p*-aminocinnamate, m.p. 139°; *Et* *p*-cyanobenzylidene-*p*-aminocinnamate, m.p. 154° and 182°; *Me* furfurylidene-*p*-aminocinnamate, m.p. 108°; the condensation product of CHO·C₆H₄·CH:CH·CO₂Et and NH₂·C₆H₄·CH:CH·CO₂Et, amorphous liquid $\xrightleftharpoons{206^\circ}$ cryst. liquid I (*Bz* form) $\xrightleftharpoons{194^\circ}$ cryst. liquid II (*Rs* form) $\xrightleftharpoons{131^\circ}$ cryst. solid II (also cryst. liquid II \rightarrow cryst. solid I \rightarrow cryst. solid II). H. W.

Application of the Strecker reaction to synthesis of hydroxyalkylamino-acids. β -Amino- γ -methylbutan- γ -ol and cyclohexanone. M. K. USCHENKO (Ukrain. Chem. J., 1938, **13**, 6—9).— β -Amino- γ -methylbutan- γ -ol hydrochloride, cyclohexanone, and KCN in aq. EtOH (48 hr. at room temp.) yield 1-cyano-1-(β -hydroxy- α - β -dimethylpropylamino)cyclohexane, m.p. 74—75° (hydrochloride, m.p. 185—187°), hydrolysed to 1-(β -hydroxy- α - β -dimethylpropylamino)cyclohexanecarboxylic acid, m.p. 284—288° (hydrochloride, m.p. 256—259°). R. T.

Benzoic acid and vanadium pentoxide. J. F. LEVY (Bol. Soc. Quím. Peru, 1937, **3**, 217—218).—Excess of BzOH with V₂O₅ at 249° yields *V* benzoate, OH·V(OBz)₂. F. R. G.

Electrolysis of 2 : 4-dimethylbenzoic acid in presence of its sodium salt in methyl alcohol. F. FICHTER, H. STENZL, and E. BEGLINGER (Helv. Chim. Acta, 1938, **21**, 375—380).—Electrolysis of 2 : 4-C₆H₃Me₂·CO₂H and 2 : 4-C₆H₃Me₂·CO₂Na in abs. MeOH. with Pt anode and Cu cathode at 35—40° is mainly an oxidation leading to 5-methylphthalide (I), m.p. 119° [whence 3-hydroxymethyl-*p*-toluic acid,

m.p. 130° when rapidly heated or m.p. 118° with formation of (I) when slowly heated], 3:3'-dimethyl-dibenzyl-6:6'-dicarboxylic acid, m.p. 284° [Ba salt; characterised by oxidation to 1:2:4-C₆H₃(CO₂H)₃], a little *m*-xylene (II), and less *m*-xylenol (III). The same substances except (II) and (III) are obtained by oxidation with K₂S₂O₈. H. W.

Action of thionyl chloride and sulphur dichloride on methyl salicylate. J. A. KUNDARGI, Y. M. CHAKRADEO, and S. V. SHAH (J. Univ. Bombay, 1937, 6, Part II, 82—84; cf. A., 1937, II, 17).—Me salicylate and SOCl₂ (or SCl₂) (2 mols.) react in presence of Zn, Fe, BiCl₃, ZnCl₂, SnCl₂, SbCl₃, and FeCl₃ as catalysts; 1 mol. of SOCl₂ is used, the other being swept away with the HCl. SCl₂ is not formed in the first stage. F. R. S.

Amino-ethers of hydroxybenzoic esters. C. ROHMANN and A. KOCH (Arch. Pharm., 1938, 276, 154—164).—The appropriate ester of *p*-OH·C₆H₄·CO₂H with CH₂Cl·CH₂·NEt₂·HCl and KOH in COMeEt or COMe₂ yields the following: Me (hydrochloride, m.p. 146°), Et (hydrochloride, m.p. 154°), Pr^a (hydrochloride, m.p. 103°), Pr^b (hydrochloride, m.p. 146°), Bu^a [hydrochloride, (I), m.p. 74°], Bu^b [hydrochloride, (II), m.p. 92°], and allyl *p*-β-diethylaminoethoxybenzoate [hydrochloride, m.p. 176—177° (decomp.)]. All the hydrochlorides are local anaesthetics, (I) and (II) being most powerful with twice the activity of cocaine. J. D. R.

Chloral-amides. IV. Reactivity of α-hydroxyl group in chloral-nitrosylcarbamides. N. W. HIRWE and (Miss) K. D. GAVANKAR (J. Univ. Bombay, 1937, 6, Part II, 123—126).—The chloral-nitrosylcarbamides [nitrosalicyl-βββ-trichloro-α-hydroxyethylamides] with Ac₂O in H₂SO₄ give Ac₂ derivatives but in alkaline medium, anhydro-derivatives are formed. BzCl in NaOH forms Bz₂, whilst Me₂SO₄ similarly yields α-OMe-, derivatives. The following are described: α-methoxychloral-3-nitro-, m.p. 114°, and -5-bromo-3-nitro-2-hydroxybenzamide, m.p. 115—116°; α-acetoxychloral-3-nitro-, m.p. 151—152°, and -5-bromo-3-nitro-2-acetoxychloral-3-nitro-, m.p. 168°; α-methoxychloral-3:5-dinitro-2-hydroxybenzamide, m.p. 172°; α-benzoyloxychloral-3:5-dinitro-2-benzoyloxybenzamide, m.p. 196—197°; α-acetoxy-, m.p. 168—169°; -benzoyloxy-, m.p. 175—176°, and -methoxychloral-5-nitro-2-methoxybenzamide, m.p. 144°; α-anhydro-di(chloral-5-nitro-2-methoxybenzamide), m.p. 207—208°; α-methoxy-, m.p. 104—105°, and -acetoxychloral-3-nitro-2-methoxybenzamide, m.p. 94—95°; α-acetoxychloral-3:5-dinitro-2-methoxybenzamide, m.p. 172°; and anhydro-di(chloral-3-nitro-2-methoxybenzamide), m.p. 153—154°. F. R. S.

New synthetic method in the pyrazole group. II. Behaviour of malonic acid derivatives in attempted pyrazole syntheses. R. JUSTONI (Gazzetta, 1938, 68, 49—59; cf. A., 1937, II, 261).—CN·CHNa·CO₂Et with CPhCl·N·NHPh (I) gives, not a pyrazole, but β-benzoyl-α-cyanoacetyl-α-phenylhydrazine (II), m.p. 176·5°, converted by alkali into NHPh·NHBz (III) (using Na₂CO₃, CN·CH₂·CO₂H is also detected). With KCN the chloroacetyl compound corresponding with (II) gives only a 1:3:4-

oxadiazine (cf. A., 1928, 1386); but (II) is obtained from (III) and CN·CH₂·COCl. With CHNa(CO₂Et)₂, (I) gives β-benzoyl-α-carbethoxyacetyl-α-phenylhydrazine, m.p. 132°; also obtained from (III) and CO₂Et·CH₂·COCl. The mechanism of formation of the above compounds is discussed; an intermediate 1:3:4-oxadiazole is suggested. E. W. W.

Mechanism of chemiluminescence of 3-amino-phthalhydrazide. B. TAMAMUSHI and H. AKIYAMA (Z. physikal. Chem., 1938, B, 38, 400—406).—The intensity of the luminescence produced by H₂O₂ + hæmin is diminished by adding benzoquinone (I). In presence of quinol the appearance of the luminescence is delayed for several min., i.e., until (I) is formed. Addition of aq. TiCl₃ or Na₂S₂O₄ will momentarily intensify the luminescence produced by O₂ in presence of hæmin. H₂ in presence of colloidal Pd produces a similar result. The ultra-violet absorption spectrum shows that during the oxidation the enol form of the hydrazide disappears, a phthalic acid being produced. The mechanism of the oxidation is discussed. H. J. E.

Olivil and isoolivil. B. L. VANZETTI (Mem. R. Accad. Ital., 1937, 8, 411—443).—Previous work (A., 1912, i, 353; 1931, 226; 1934, 1099; 1936, 842) is recapitulated. Dimethylisoolivilic acid, an intermediate in the oxidation of isoolivil Me₂ ether to the substituted phthalide and benzoylbenzoic acid (*loc. cit.*), is regarded as 4-hydroxy-6:7:3':4'-tetramethoxy-1-phenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic acid, m.p. about 230°, [α]_D²⁵ +43·9°. The relation of olivil and isoolivil to other natural products, and their respective steric configurations, are discussed. E. W. W.

Synthesis and properties of phenylcyclohexyl-acetaldehyde. E. D. VENUS-DANILOVA and A. I. BOLSCHUCHIN (J. Gen. Chem. Russ., 1937, 7, 2823—2830).—CH₂Ph·CN in C₆H₆ is boiled with NaNH₂ until evolution of NH₃ ceases, and then with bromocyclohexane, to yield cyclohexylphenylacetone, m.p. 55—56°, hydrolysed by hot 85% H₂SO₄ to cyclohexylphenylacetamide, m.p. 172—173°, and -acetic acid, m.p. 150—151° [Ca salt, +H₂O; chloride (I), b.p. 157—158°/10 mm.; anhydride, m.p. 123—124°]. (I) in C₆H₆ is reduced by H₂ in presence of Pd catalyst to cyclohexylphenylacetaldehyde, b.p. 167—170°/18 mm. (semicarbazone, m.p. 161—162°; oxime, m.p. 118°; phenylhydrazone, m.p. 122—123°), together with α-cyclohexyl-α-phenylethane, b.p. 132—133°/18 mm. R. T.

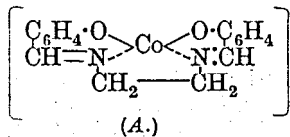
Odoriferous constituent of green tea. X. Synthesis of *p*-hydroxycinnamaldehyde. S. TAKEI, Y. SAKATO, and M. ONO (Bull. Inst. Phys. Chem. Res. Japan, 1938, 17, 216—225).—*p*-OMe·C₆H₄·CHO and MeCHO afford *p*-OMe·C₆H₄·CH:CH·CHO which with AlCl₃ gives *p*-hydroxycinnamaldehyde, m.p. 140° [oxime, m.p. 165°; semicarbazone, m.p. 240°; phenylhydrazone, m.p. 172°; *p*-nitrophenylhydrazone, m.p. 243° (Ac derivative, m.p. 225°); 2:4-dinitrophenylhydrazone, m.p. 278°; Ac derivative, m.p. 83°; Bz derivative, m.p. 107°], and is reduced (OEt·MgCl) to *p*-OMe·C₆H₄·CH:CH·CH₂·OH (3:5-dinitrobenzoate,

m.p. 117°; 4'-iododiphenylurethane, m.p. 201°), demethylation (AlCl_3 or HBr) of which gives no $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$. Bouveault reduction of $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ yields $\gamma\text{-p-anisyl-n-propyl alcohol}$, b.p. 128°/2 mm. (3:5-dinitrobenzoate, m.p. 74°; 4'-iododiphenylurethane, m.p. 162°), demethylated (HBr) to $\gamma\text{-p-hydroxyphenyl-n-propyl alcohol}$, b.p. 170°/2 mm. (3:5-dinitrobenzoate, m.p. 149°; 4'-iododiphenylurethane, m.p. 178°). Demethylation of $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$ affords $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$, m.p. 109° (semicarbazone, m.p. 210°), which is a possible odoriferous constituent of tea. F. N. W.

Cannizzaro's reaction in heavy water.—See A., 1938, I, 261.

Some compounds in which bromine is more electronegative than chlorine. M. BETTI (IX Congr. intern. quim. pura apl., 1934, 4, 317—320).—Anomalies in $[M]_D$ for the condensation products of $o\text{-C}_6\text{H}_4\text{Br}\cdot\text{CHO}$ and $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ with $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHPh}\cdot\text{NH}_2$ are held to suggest that there may be a class of compounds in which Br is more electronegative than Cl. CH. ABS. (r)

Partial valency cyclic compounds. IV. Inner complex cobalt salts of hydroxyaldimines. T. TSUMAKI (Bull. Chem. Soc. Japan, 1938, 13, 252—260; cf. A., 1937, II, 247).—The reddish-brown Co^{II} salicylaldehyde-ethylenedi-imine (I) (A., 1933, 824) is stable in absence of air, but absorbs about 0.33 O_2 to yield a black oxide, which regenerates (I) at 100°. This oxidation could not be effected in solvents owing to formation of Co^{III} salts. A red solvate, $+\text{CHCl}_3$, of (I) regenerates (I) at 100° and gives the oxide in air. When kept in CHCl_3 in air, (I) gives the dark violet hydroxide (A) (X = OH), decomposed by X acid or alkali, but a solution in MeOH-N-AcOH with aq. NH_4Cl affords the chloride (X = Cl). Absorp-



tion spectra of (I), its oxide, and the hydroxide confirm the structures assigned and indicate that the O are *trans* to each other, thus necessitating the *as*-structure for (I). R. S. C.

Prototropy in relation to the exchange of hydrogen isotopes. IV. Isomerisation and exchange in methyleneazomethines. E. DE SALAS and C. L. WILSON (J.C.S., 1938, 319—321).—Measurements are recorded of rates of isomerisation and isotopic H exchange of the tautomerides: $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{N}\cdot\text{CHPh}$ (I) \rightleftharpoons $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\text{Ph}$ (II) (cf. Ingold and Shoppee, A., 1929, 927). Each was allowed to isomerise in EtOH containing NaOEt-EtOD (cf. A., 1936, 1344), and the azomethines were analysed for isomeric composition and D content. Experiment shows that exchange, for (II) and possibly for (I), occurs faster than isomerisation. It is suggested that an additional mechanism of exchange exists involving direct replacement of the mobile H by D without isomerisation, and the stereochemical course of this reaction is considered. A. T. P.

Addition reactions of the azomethine group. D. PHILPOTT and W. J. JONES (J.C.S., 1938, 337—341).—The reactivity of the azomethine group in anils and indolenines is investigated. *Et* 2-anilinomethyl- (I), m.p. 53°, *Et* 2- α -anilinobenzyl- (II), m.p. 88°, and *Et* 2- α -2'-naphthylaminobenzyl- (III), m.p. 111°, -cyclopentanone-2-carboxylates are obtained from $\text{CH}_2\cdot\text{NPh}$ (IV), $\text{CHPh}\cdot\text{NPh}$ (in EtOH), and $\text{CHPh}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7$ (in C_6H_6), respectively, and *Et* cyclopentanone-2-carboxylate (V). (II) and (III) are converted by refluxing in AcOH-EtOH into *Et* 2-phenyl-3:4-trimethylene-2:3-dihydroquinoline-3-carboxylate, m.p. 102°, and *Et* 3-phenyl-1:2-trimethylene-2:3-dihydro- β -naphthaquinoline-2-carboxylate, m.p. 130°, respectively, and are also obtained directly from (V) and the azomethines; (I) does not react similarly. (I) and α - or β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ in C_6H_6 yield 2-anilinomethyl- α -naphthol (VI), m.p. 117° (*Ac* derivative, m.p. 127°), and 1-anilinomethyl- β -naphthol (VII), m.p. 132° (*Ac* derivative, m.p. 176°), which with $\text{EtOH-NHPh}\cdot\text{NH}_2$ give 2-phenylhydrazino- α -, m.p. 106°, and 1-phenylhydrazino- β -, m.p. 206° (decomp.), -naphthol, respectively. $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}$ and $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ similarly give 1- α -anilino-*cinnamyl*- β -naphthol, m.p. 218°. (IV) and α - or β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$, or alternatively (VI) and (VII), and PhCHO in EtOH yield 2:3-diphenyl-2:3-dihydro-1:3- α -, m.p. 150°, and -2:4- β -, m.p. 140°, -naphthoxazine, respectively. α -Aminocamphor and (V) in aq. NaOAc-AcOH yield *Et* 2-camphoryliminocyclopentane-1-carboxylate, m.p. 129°. The monophenylhydrazones of 1:3-diketo-2-methyl- and -2-phenyl-hydrindene and anhyd. ZnCl_2 in EtOH give 3-methyl-, m.p. 175°, and 3-phenyl-, m.p. 225°, -2:3-*o*-benzoyleneindolenines, respectively. (IV) does not react with RCOCl or $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$. A. T. P.

Reactions of glyoxals with amino-acids. S. KOBAYASI (J. Biochem. Japan, 1938, 27, 107—118).— NH_2 -acids convert BzCHO into PhCHO or its condensation product and this reacts with the NH_2 liberated to give 2:4:5-triphenyloxazole. The reactivity of NH_2 -acids with AcCHO increases with the distance between NH_2 and CO_2H . Dipeptides are more reactive than α -monoamino-acids which, in turn, are more reactive than the monoaminodicarboxylic acids. These facts, together with increased activity when the CO_2H is esterified, indicate the inhibitory influence of the CO_2H . With $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, the *o*- and *m*-isomerides are approx. equally reactive and the *p*-isomeride is least reactive. F. O. H.

$\alpha\delta$ -Dimesitylbutanones. R. E. LUTZ and J. L. WOOD (J. Amer. Chem. Soc., 1938, 60, 713—716).— $\alpha\delta$ -Dimesitylbutan- α - (I), m.p. 105—105.5°, and - β -one (II), m.p. 118—119° (2:4-dinitrophenylhydrazones, m.p. 187.5—188°; semicarbazone, m.p. 177.5—178°; oxime, m.p. 154.5—155°), are synthesised and their structures are proved. α -Hydroxy- $\beta\gamma$ -oxido- $\alpha\delta$ -dimesitylbutan- δ -one, prepared from the dione oxide by $\text{H}_2\text{-Pt}$, is further hydrogenated (Raney Ni) to α -hydroxy- $\alpha\delta$ -dimesitylbutan- δ -one (III), which is oxidised by CrO_3 to $(\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2)_2$ (IV) and reduced by Na-EtOH in N_2 to $\alpha\delta$ -dimesitylbutane- $\alpha\delta$ -diol, m.p. 184.5—185.5°, also obtained similarly from

(IV). I-HI-red P-AcOH converts the diol into $\alpha\delta$ -dimesitylbutane (V), m.p. 125.5—126°. I-red P-AcOH merely dehydrates (III) to $\alpha\delta$ -dimesityl- Δ^8 -buten- α -one (VI), m.p. 116.5—117.5° (no oxime or dinitrophenylhydrazone), whereas HCl-Et₂O or, better, PCl₅ in CHCl₃ gives δ -chloro- $\alpha\delta$ -dimesitylbutan- α -one, m.p. 102.5—103°, hydrolysed to (III) by C₅H₅N and converted into (VI) by heating alone at 130° or by boiling in AcOH. Hot KOH-MeOH removes HCl from the Cl-ketone to give $\alpha\delta$ -dimesityl- Δ^7 -buten- α -one, m.p. 114°, which rearranges to (VI) in hot HCl-AcOH and resists hydrogenation. Hydrogenation of the Cl-ketone or (VI) yields (I), which gives no CO-derivatives. Na-EtOH reduces (I) or (VI) to $\alpha\delta$ -dimesitylbutan- α -ol, m.p. 147.5—148° (II), best obtained from C₆H₂Me₃·CH(OH)·CO·CH₂C(OH)·C₆H₂Me₃ by Sn-HCl (cf. also Lutz, A., 1938, II, 193), is reduced by Na-EtOH in N₂ to $\alpha\delta$ -dimesitylbutan- β -ol, m.p. 125.5—126° (phenylurethane, m.p. 122—122.5°). The iodide, m.p. 105.5—106°, prepared therefrom by red P-AcOH-HI, is reduced by Na-EtOH to (V). M.p. are corr. R. S. C.

Benzophenone from diphenylmethane. S. M. RIVKIN (J. Appl. Chem. Russ., 1938, 11, 83—84).—CH₂Ph₂ in aq. Pb(OAc)₂ and HNO₃ (5 hr. at the b.p.) give CPh₂ in 80—90% yield. R. T.

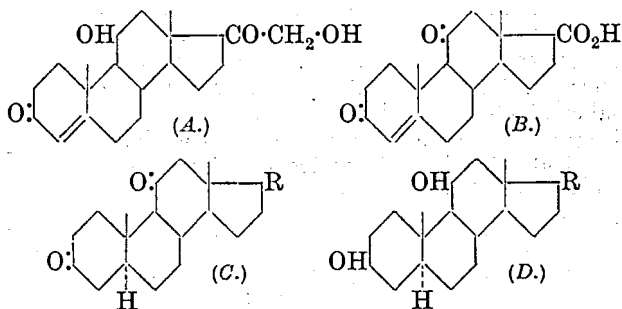
Synthesis of 4-keto-10-methoxy-1:2:3:4-tetrahydrophenanthrene. H. WAHL (Compt. rend., 1938, 206, 683—685; cf. A., 1938, II, 144).—Me sodio-3-methoxy-2-naphthoyleacetate (cf. *ibid.*, 143) with CH₂Br·CO₂Me affords Me₂ 3-methoxy-2-naphthoylesuccinate, m.p. 118°, which with boiling dil. H₂SO₄ affords β -(3-hydroxy-2-naphthoyle)propionic acid (I), m.p. 202° (Me ester, m.p. 105°), converted by Me₂SO₄ into Me β -(3-methoxy-2-naphthoyle)propionate, m.p. 83.5° (lit. 87°) (p-nitrophenylhydrazone, m.p. 166°), and β -(3-methoxy-2-naphthoyle)propionic acid, m.p. 161° (lit. 164°) [p-nitrophenylhydrazone, m.p. 187° (decomp.)]. (I) when reduced (Clemmensen) gives γ -(3-hydroxy-2-naphthyl)butyric acid, m.p. 131° [Me ether (II), m.p. 94° (lit. 98°) (Na salt)]. (II) is cyclised (P₂O₅ in C₆H₆) to 4-keto-10-methoxy-1:2:3:4-tetrahydrophenanthrene, m.p. 83° (lit. 87°) [oxime, m.p. 165° (lit. 160°); p-nitrophenylhydrazone, m.p. 170°]. J. L. D.

Microscopic investigations of polymorphous substances. I. Benzil, 8-hydroxyquinoline, and benzidine. L. KOFLER and E. LINDEPAINTNER (Mikrochem., 1938, 24, 43—58).—Micro-m.p. determinations show the following nos. of modifications: benzil, three, m.p. 95°, 41.5°, 27°; 8-hydroxyquinoline, four, m.p. 73.5°, 65°, 57—58°, 38—39.5°; benzidine, five, m.p. 129°, 125°, 120.5—121°, 116.5—117°, fifth m.p. not determined. O. J. W.

Sterol group. XXXV. Bromination of 7-ketocholestanyl acetate. T. BARR, I. M. HEILBRON, E. R. H. JONES, and F. S. SPRING (J.C.S., 1938, 334—337; cf. A., 1937, II, 344).—7-Ketocholestanyl acetate (I) is not brominated in AcOH at 20°, but in CHCl₃ at 20° gives the α -6-Br-derivative (II), m.p. 173—175°, [α]_D²⁰ +35° (rotations in CHCl₃), converted by MeOH-KOH into 3:6-dihydroxy-7-ketocholest-

ane, m.p. 148—150° (softens at 140°) (dibenzoylate, m.p. 184—186°). From the COMe₂ mother-liquor of (II), or from (II) and AcOH-HBr, β -6-bromo-7-ketocholestanyl acetate (III), m.p. 142—143°, [α]_D²⁰ -8.8°, is obtained. The constitutions of (II) and (III) are established by conversion [(II) readily] into 7-keto-3-acetoxy- Δ^5 -cholestene (IV) and 7-keto- $\Delta^3:5$ -cholestadiene by treatment with C₅H₅N. AgNO₃-C₅H₅N and (II) give (IV), but (III) yields 6:7-diketocholestanyl acetate, indicating that in (II) the C₅-H and C₆-Br are *cis*, and in (III), *trans*. (I) and Br (2 mols.) in CHCl₃ at 20°, or (II) or (III) and Br (1 mol.) in HBr-AcOH, give a dibromo-7-ketocholestanyl acetate, m.p. 176—177°, [α]_D²⁰ +38.1°. Ultra-violet absorption spectra of the Br₁- and Br₂-derivatives of (I) and the 6-keto-isomeride are discussed. (I) is a derivative of cholestane, since Wolff-Kishner reduction of the semicarbazone of 7-ketocholestanol gives cholestanol. A. T. P.

Constituents of the adrenal gland. XV. Transformation of corticosterone into allo-pregnane. XVI. Synthesis of Δ^4 -pregnene-20:21-diol-3-one. M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 161—171, 171—180; cf. A., 1938, II, 147).—XV. The structure (A) is



established for corticosterone (I) but uncertainties remain with regard to the position of CO at 3, of the double linking at C₄, of the *sec.* OH at C₁₁, and of the configuration at C₁₀. Oxidation of (I) with CrO₃ gives the acid (B) [probably identical with Kendall's "acid I" (A., 1936, 1117)], hydrogenated and then oxidised to the acid [(C) R = CO₂H], m.p. 279—282° (corr.; decomp.), probably identical with Kendall's acid 1A"; this does not give a cryst. derivative when treated with Zn-Hg and HCl. Complete hydrogenation of (I) (PtO₂ in EtOH-AcOH) affords allo-pregnane-3:11:20:21-tetraol, m.p. 215—218° (corr.), possibly identical with Kendall's "hexahydro-compound B"; this is oxidised by HIO₄ to the (impure) aldehyde [(D) R = CHO], transformed by MgMeBr into the triol [(D) R = CHMe·OH], m.p. 177—178° (corr.), which is oxidised to allo-pregnane-3:11:20-trione [(C) R = COMe], m.p. 212—216° (corr.), [α]_D²⁰ +133±2° in abs. EtOH, reduced (Clemmensen) to allo-pregnane, m.p. 84.5—85°, [α]_D²¹ +12.7° in CHCl₃. This hydrocarbon is also obtained from deoxycorticosterone acetate [Δ^5 -3-hydroxy-21-acetoxypregnen-20-one] by successive reduction and hydrolysis, oxidation with HIO₄, treatment with MgMeBr, oxidation with CrO₃, and reduction with Zn-Hg.

XVI. In an attempt to decide whether the presence

of the ketol group in the side chain is necessary for the development of cortin activity it is shown that Δ^4 -pregnene-20:21-diol-3-one (II) [= (A) with $\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ for $\text{CO}\cdot\text{CH}_2\cdot\text{OH}$] is at most one third as active as (I) or deoxycorticosterone. Δ^5 -3-Hydroxy-21-acetoxypregnen-20-one is hydrolysed and reduced by $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH to Δ^5 -pregnene-3:20:21-triol, m.p. 206—216°, transformed by COMe_2 containing anhyd. CuSO_4 into the 20:21-isopropylidene ether, m.p. 166—169° (corr.), $[\alpha]_D^{25} -50.8^\circ \pm 3^\circ$ in COMe_2 ; this is converted by Oppenauer's method into Δ^4 -pregnene-20:21-diol-3-one isopropylidene ether, α -form, m.p. 126° (corr.), $[\alpha]_D^{20} +91.5^\circ \pm 1^\circ$ in COMe_2 , β -variety, m.p. 132° (corr.), $[\alpha]_D^{20} +70.5^\circ \pm 1.5^\circ$ in COMe_2 . Removal of CMe_2 leads to (II), α -form, m.p. 166—167° (corr.), $[\alpha]_D^{20} +92.6^\circ \pm 1^\circ$ in abs. EtOH, β -variety, m.p. 183—185° (corr.), respectively. H. W.

Dimorphism of nitrobenzylidenephthalide and its isomerides, nitrodiketophenylhydrindene and nitroisobenzylidenephthalide. I. KEIMATSU (J. Pharm. Soc. Japan, 1933, 53, 1248—1265).—Thermal decomp. of dinitrobenzylidenephthalide,

$\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C}(\text{NO}_2)\cdot\text{CHPh}\cdot\text{NO}_2$, gives α -nitrobenzylidenephthalide (I), m.p. 195°, and a substance, m.p. 147°, now identified as a metastable form of (I). 2-Nitro-1:3-diketo-2-phenylhydrindene, m.p. 118—122° (decomp.), is formed by passing N_2O_3 into a C_6H_6 solution of 1:3-diketo-2-phenylhydrindene. N_2O_3 reacts with isobenzylidenephthalide in C_6H_6 to give two forms of nitroisobenzylidenephthalide [4-nitro-3-phenylisocoumarin], m.p. 154° and m.p. 235°.

CH. ABS. (r)

Action of selenium dioxide on sterols and bile acids. IV. Cholestane-2:3-dione from cholestan-3-one. E. T. STILLER and O. ROSENHEIM (J.C.S., 1938, 353—357).— SeO_2 is used to oxidise saturated and unsaturated steroid ketones to α -diketones. Cholestanone [o-tolylsemicarbazone, m.p. 228—229° (decomp.)] (1 part) and SeO_2 (8 parts) in aq. EtOH give 30% of cholestane-2:3-dione (I) [quinoxaline derivative (II), m.p. 179—180°, from $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$]. (I) occurs in two interconvertible modifications, probably tautomeric enolic forms, m.p. 144—145° (A), $[\alpha]_{461}^{20} +91.5^\circ$, $[\alpha]_D^{20} +79.1^\circ$, and m.p. 168—169° (B), $[\alpha]_{461}^{22} +67.3^\circ$, $[\alpha]_D^{22} +57.2^\circ$. (A) and AcOH and a little HCl at 100° (bath) give (B), reconverted into (A) through the K salt, prepared by aq. KOH at 0°. (A), (B), and an equimol. mixture, m.p. 130—132°, all give (II), and are oxidised by H_2O_2 in aq. KOH-EtOH to the same dicarboxylic acid, $\text{C}_{27}\text{H}_{46}\text{O}_4$, m.p. 194—195°. (A) and (B), however, yield different enolic monoacetates, m.p. 137—138°, $[\alpha]_{461}^{25} +109.8^\circ$, $[\alpha]_D^{25} +91.8^\circ$, and m.p. 140—144°, respectively. The monobenzoate of (A) is dimorphous; in polarised light, both forms (interconvertible) melt to an anisotropic liquid at 162—163°, changing to the isotropic melt at 193—194°. (B) is identical with the diketone obtained by debrominating 2:4-dibromocholestanone (Inhoffen, A., 1937, II, 423). Cholestanone, amyl formate, and Na in Et₂O give hydroxymethylenecholestan-3-one, m.p. 182—184°, clearing at 195°. Δ^4 -Cholesten-3-one, cholestan-3-ol-6-one,

cholestan-6-one, cholestane-3:6-dione, Δ^4 -cholestene-3:6-dione, and 3:12-diketocholelanic acid react with SeO_2 in AcOH (not in EtOH) at 100°, but cholestan-3-ol-7-one acetate, $\Delta^{3:5}$ -cholestadien-7-one and 12-ketocholelanic acid do not. All rotations are in CHCl_3 . Absorption spectra for (I) are given. A. T. P.

$\alpha\delta$ -Dimesitylbutane- $\alpha\beta\delta$ -trione enol and its reduction products. R. E. LUTZ and J. L. WOOD (J. Amer. Chem. Soc., 1938, 60, 705—713).— $\alpha\delta$ -Mesityl groups almost entirely suppress the tendency of $\alpha\beta\delta$ -triketones to form furan derivatives. Complex tautomerism is evidenced by many of the reactions described below. (2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}$)₂ and Br in AcOH give the dibromide (I), which with dil. NaOH in 80% MeOH loses HBr and undergoes hydrolysis to β -hydroxy- $\alpha\delta$ -diketo- $\alpha\delta$ -dimesityl- Δ^2 -butene (II) (60—65%), the triketonic form of which is unknown. This reacts rapidly with Br and FeCl_3 , is a strong acid, giving an insol. Na salt when shaken in light petroleum with aq. Na_2CO_3 , and gives a semicarbazone, m.p. 204°, mono-oxime, m.p. 170.5—171°, and 2:4-dinitrophenylhydrazone, m.p. 234—235°, but gives no quinoxaline derivative and is unaffected by HCl-MeOH, AcCl and a trace of H_2SO_4 , or HCl-AcOH-PhMe. HNO_3 gives a small amount of a non-enolic substance, m.p. 177—180° (uncorr.). With $\text{AcCl}\cdot\text{C}_5\text{H}_5\text{N}$ it gives, instead of the usual furanone, the enol acetate, m.p. 144.5—145°, previously (A., 1927, 59) supposed to be the triketonic form of (II). The structure of the acetate is shown by alkaline hydrolysis to (II), synthesis from (I) by NaOAc, and hydrogenation (PtO_2) in EtOH to $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$. With Zn-AcOH at 30°, 80°, or 100° (II) gives $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_2\text{Me}_3$, 25% of ($\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2$)₂ (III) being also formed at 100°. With Zn-80% EtOH- NH_4Cl at 40—50° (II) gives 88% of $\alpha\delta$ -dihydroxy- γ -keto- $\alpha\delta$ -dimesityl- Δ^2 -butene (IV), m.p. 104.5—105.5°; Zn-HCl-78% EtOH affords $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Me}_3$ and (III); Sn-HCl-AcOH gives 20—40% of $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{C}_6\text{H}_2\text{Me}_3$, 5% of (III), and other products; red P-I-AcOH gives (III). Hydrogenation of (II) using Pd-BaSO₄, Pt, or Raney Ni in 95% EtOH gives the trienol, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{C}_6\text{H}_2\text{Me}_3$ (V), which is not isolated as it passes in air into (II) or by rearrangement, when kept, into (IV); small amounts of (III) are also sometimes obtained. With CH_2N_2 (II) yields trans- $\alpha\delta$ -diketo- β -methoxy- $\alpha\delta$ -dimesityl- Δ^2 -butene (VI), m.p. 113—114°, with some (? cis-) (VII), m.p. 151—152°, and (?-trans-) $\gamma\delta$ -diketo- α -methoxy- $\alpha\delta$ -dimesityl- Δ^2 -butene (VIII), m.p. 127—128°. (VII) passes into (VIII) in light, in hot 1% KOH-MeOH, or when distilled at 150°/vac., and absorbs 2 H in presence of Pt to give a colourless solution from which it is regenerated by I. Methylation of (IV) and subsequent oxidation in KOH-MeOH yields (VIII), which is stable to KOH-MeOH and NaOMe, is equilibrated with (VI) by NaOH, and is obtained from (VI) in light, and is reduced by Zn- NH_4Cl -aq. MeOH to a colourless solution from which it is regenerated by I. (IV) gives a Na salt with NaOH, but not with Na_2CO_3 , gives a red FeCl_3 colour, and absorbs Br;

with Ac_2O and a little H_2SO_4 it gives 3-acetoxy-2:5-dimesitylfuran; with 2:4-(NO_2) $_2\text{C}_6\text{H}_3\text{NH}\cdot\text{NH}_2$ it gives a substance ($\text{N}=21.6\%$), m.p. 115—116°, and with HNO_3 a non-enolic substance, m.p. 152—159°; it gives no semicarbazone or oxime, yields gums with CrO_3 or AcCl , and is not rearranged by AcOH . In air at 200° (IV) gives (II), but at 200° in absence of air or with hot 10% NaOH gives, by disproportionation, (II) and (III); disproportionation probably occurs by way of $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ (IX) and $(\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH})_2$ (X); (X) and (IV) at 200° in N_2 give only poor yields of (II) and (III), but substitution of α -diketo- α -di(bromomesityl)- Δ^8 -butene for (X) gives good yields. Pyrolysis of mixtures of (IX) and (II) was without effect. Thus, (IV), (IX), and the trienol (V) are tautomeric. Reduction of (IV) by I-red P gave erratic results. With CH_2N_2 (IV) gives δ -hydroxy- γ -keto- α -methoxy- α -dimesityl- Δ^8 -butene, m.p. 149—150°, which in air at 200° gives (VIII) and with O_3 in CHCl_3 affords with difficulty $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{Me}$ [(NO_2) $_2$ -derivative, m.p. 140.5—141°]. With $\text{Zn}\cdot\text{HCl}$ -88% EtOH (IV) gives α -hydroxy- γ -keto- α -dimesityl- Δ^8 -butene (XI), m.p. 103.5—104.5° (oxime, m.p. 125—125.5°), stable to hot alkali, HI-red P, and $\text{Sn}\cdot\text{HCl}$, and ozonised to $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$ and $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. CH_2N_2 converts (XI) into its *Me ether*, m.p. 148.5—149.5° [oxime, m.p. 182—186° (uncorr.)] (with small amounts of an isomeride, m.p. 135—136.5°, and a substance, m.p. 175—176°), converted by O_3 with difficulty into $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{Me}$. M.p. are corr.

R. S. C.

Reaction between methylated quinones and sodium enolates. VIII. Mechanism. Addition of sodium malonic ester to a methylene quinone. L. I. SMITH and J. W. HORNER, jun. (J. Amer. Chem. Soc., 1938, 60, 676—678; cf. A., 1937, II, 293).—Dehydro-1-methyl- β -naphthol, $\text{CH}_2(\text{CO}_2\text{Et})_2$, and NaOEt in EtOH give *Et* 5:6-benz-3:4-dihydrocoumarin-3-carboxylate, m.p. 110.5—112°, oxidised by $\text{FeCl}_3\cdot\text{HCl}\cdot\text{EtOH}$ to *Et* 5:6-benzcoumarin-3-carboxylate (I), m.p. 113—114°, and obtained therefrom by H_2 -Raney Ni in EtOH at 3 atm. This condensation supports the theory that reaction of duroquinone with $\text{CH}_2(\text{CO}_2\text{Et})_2$ involves the methylene quinone and is based on the arguments of Pummerer and Cherbuliez (A., 1919, i, 439). (I) is synthesised from 2:1-OH- $\text{C}_{10}\text{H}_6\cdot\text{CHO}$, b.p. 179—180°/22 mm., m.p. 79—81.5°, $\text{CH}_2(\text{CO}_2\text{Et})_2$, and a little piperidine at 100°.

R. S. C.

Synthesis of homonuclear hydroxymethyl-anthraquinones. H. WALDMANN and (FRL.) P. SELLNER (J. pr. Chem., 1938, [ii], 150, 145—152).—*o*-Cresol, *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$, and $\text{AlCl}_3\cdot\text{NaCl}$ at 120—130° and then at 165° give mainly 2-hydroxy-3-methyl- (I), m.p. 302°, with some 1-hydroxy-2-methyl- and 2-hydroxy-1-methyl-anthraquinone, new m.p. 238° (Ac derivative, new m.p. 184°; *Me ether*, m.p. 166°), and mixed keto-acids. These acids in conc. H_2SO_4 at 155° readily give (I). From (I) are prepared the *Me ether*, new m.p. 197°, 1- NO_2 -, new m.p. 276° (decomp.), and 1- NH_2 -derivative, new m.p. 224° (decomp.), and 3-methyl-2'-phenyloxazolo-[4':5':1:2]-anthraquinone, m.p. 288°. *m*-Cresol gives similarly

1-hydroxy-3-methyl- (*Me ether*, new m.p. 190°) and some 3-hydroxy-1-methyl-anthraquinone (II), m.p. 295° (Ac derivative, m.p. 135°; *Me ether*, m.p. 145°). Nitration etc. of (II) affords the 4- NO_2 -, m.p. 247—248° (decomp.), 4- NH_2 -, m.p. 237—238° (decomp.), 2:4-(NO_2) $_2$ -, m.p. 237—238° (decomp.) [oxidised to *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$], and 2:4-(NH_2) $_2$ -derivative, m.p. 236—237° (decomp.) (*hydrochloride*), and the phenyloxazole derivative, m.p. 201—202°. *p*-Cresol affords 1-hydroxy-4-methylanthraquinone. 1:5:2- $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{OH}$ gives 4-chloro-1-hydroxy-2-methylanthraquinone, m.p. 177—179° (Ac derivative, m.p. 188°). 1:2:5- $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{OH}$ gives 4-chloro-1-hydroxy-3-methylanthraquinone, m.p. 174°.

R. S. C.

Anthraquinone derivatives.—See B., 1938, 354.

Syntheses in the naphthacene series: naphthacenediaquinone. C. DUFRASSE and J. HOUPIL-LART (Compt. rend., 1938, 206, 756—759).—Cyclisation of $\text{CHPh}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CHPh}$ or the anhydride with H_2SO_4 (70°; 1 hr.) gives naphthacenediaquinone (I), m.p. 322° [naphthacene-5:11-quinone: the known 5:12-quinone is termed the *antioquinone* (II)], reduced to naphthacene by pyrolysis with Zn and converted by alkaline fusion in air into the same dihydroxynaphthacenequinone (III) as is similarly obtained from (II). The non-existence of two dihydroxyquinones is attributed to chelation. The absorption spectra of (I), (II), and (III) are recorded.

II. G. M.

Catalysis of inversion of menthone in chlorobenzene solution.—See A., 1938, 1, 258.

Terpineol from pinene. B. G. S. ACHARYA and T. S. WHEELER (J. Univ. Bombay, 1937, 6, Part II, 134—135).—The best conditions for obtaining terpineol, through terpin hydrate, from pinene are described (overall yield, 36%).

F. R. S.

Racemisation and optical rotation in the camphene rearrangement. III. Elucidation of the stereochemical nature of the relation of 4-methylborneol to 4-methylisoborneol. A. I. SCHAVRIGIN (J. Gen. Chem. Russ., 1937, 7, 2754—2759).—4-Methylbornylene (I) in AcOH and ZnCl_2 (8 hr. at 55—60°) yield the acetate of 4-methylisoborneol, which is hydrolysed to 4-methylisoborneol (II), and this is oxidised to camphor; the same products are obtained when α -methylcamphene (III) is taken in place of (I). (I) obtained from (II) by Tschugaev's xanthate method is identical with that given by 4-methylborneol (IV); this, together with the above results, suggests that (II) and (IV) are stereoisomerides of the same *sec.* alcohol, of the same structure as (III).

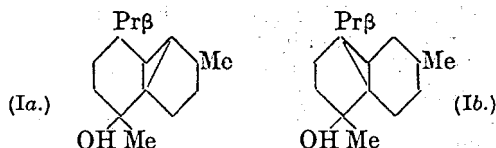
R. T.

Condensation of arylamines with the cyanohydrin of *r*-camphor and 3-methylcyclopentanone. R. D. DESAI, A. KAMAL, and S. A. NOMIN (J. Univ. Bombay, 1937, 6, Part II, 85—88).—From *r*-camphor, KCN , and the appropriate amine the following have been prepared: 1-anilino-, m.p. 152° (carbamyl derivative, m.p. 160°), 1-*p*-bromoanilino-, m.p. 162° (amide, m.p. 189°), 1-*p*-toluidino-, m.p. 143° (amide, m.p. 190°), 1- β -, m.p. 165° (amide, m.p. 182°), and 1- α -naphthylamino-1-cyanocamphane (amide, m.p.

112°). 3-Methylcyclopentanone similarly yields the following: 1-*p*-toluidino-, m.p. 66—67° (amide, m.p. 126°), 1-*p*-bromoanilino-, m.p. 69—70° (amide, m.p. 163—164°), 1- α -, m.p. 94°, and 1- β -naphthylamino-, m.p. 89° (amide, m.p. 253°), and 1-*o*-toluidino-1-cyano-3-methylcyclopentanone (amide, m.p. 89°) and the amide of 1-*m*-toluidino-1-cyano-3-methylcyclopentanone, m.p. 85°. No evidence of *cis-trans* isomerism has been found. F. R. S.

Physical identity of enantiomerides. V. Relation between the concentration and viscosity of solutions of the *d*-, *l*-, and *dl*-forms of camphor, oximinocamphors, camphorquinone, camphoric acid, and sodium camphorate. B. K. SINGH (Proc. Indian Acad. Sci., 1938, 7, A, 50—67; cf. A., 1936, I, 497).—For the *d*-, *l*-, and *dl*-forms of camphor, camphoric acid, and camphorquinone (I) in EtOH and of Na camphorate in H₂O Arrhenius' formula $(C_1 - C_2) \log A = \log \eta_1/\eta_2$, applies, best when *C* is expressed in mols. per l. of solvent. For all forms of (I) in CHCl₃ there is better constancy of *A* if *C* is expressed as mols. per litre of solution, but in this case *d* is not \propto concn. and the solution is thus not ideal. For the various forms of stable and unstable oximinocamphor Arrhenius' equation does not apply, possibly because the solutions are not ideal or owing to association; in this, but not in other cases, Kendall's cube root formula applies, although it is theoretically valid only for ideal solutions. *l*- and *d*-Forms have identical η , which is usually < that of the *dl*-form. R. S. C.

Constitution of ledum-camphor and leden. G. KOMPPA and G. A. NYMAN (Compt. rend. Trav. Lab. Carlsberg, 1938, 22, 272—274).—The constitution formerly suggested for ledum-camphor (ledol) (I) must be modified to accord with the structure of azulene (Plattner *et al.*, A., 1936, 993), which is one of the products of dehydrogenation of (I). The revised structures are either (I) *a* or *b*.

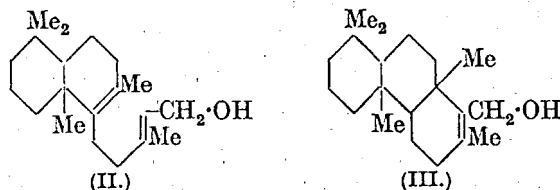


F. R. S.

Unsaturated centre of the triterpene alcohol lupeol. I. M. HEILBRON, T. KENNEDY, and F. S. SPRING (J.C.S., 1938, 329—334).—Lupeol (I), C₃₀H₅₀O, has been isolated in comparatively good yield from *Mariposa gutta* and the presence of one ethylenic linking and consequently its pentacyclic nature have been confirmed. Hydrogenation (H₂-PtO₂) of lupenyl acetate (II) yields lupanyl acetate, m.p. 245—246°, [α]_D²⁰ -1.8°, hydrolysed to lupanol (benzoate, m.p. 259—260°, [α]_D²⁰ +27.1°). Lupanone, m.p. 204—205°, [α]_D²⁰ +16.2° [oxime, m.p. 270°; hydrazone, m.p. 341—342° (decomp.); *m*-nitrobenzylidene derivative, m.p. 127°], is obtained by catalytic hydrogenation of lupenone [hydrazone, m.p. 341—342° (decomp.)], and also, along with lupanedicarboxylic acid, m.p. 272° (decomp.), by oxidation of lupanol with CrO₃. Lupenonehydrazone with NaOEt gives α -lupene, m.p. 163°, [α]_D²⁰ +30.2°, which is catalytically hydrogen-

ated to lupane, m.p. 184°, [α]_D²⁰ -1.1°, also obtained from lupanone by reduction (Zn-Hg). Lupenone is reduced (Zn-Hg) is β -lupene, m.p. 191°, [α]_D²⁰ +21.4°. Catalytic hydrogenation of lupadiene affords γ -lupene, m.p. 197—199°, [α]_D²⁰ -19.7°. Ozonolysis of (II) gives CH₂O in 18% yield, from which it follows that the ethenoid linking of (I) is present as an exocyclic CH₂ group. Ozonolysis of either β - or γ -lupene fails to give CH₂O, whereas similar treatment of α -lupene gives this aldehyde, indicating that it is the parent hydrocarbon of (I). With CrO₃ (II) affords a keto-acetate, C₃₂H₅₂O₃, m.p. 260—262°, [α]_D²⁰ +7.4°, hydrolysed to a keto-alcohol, C₃₀H₅₀O₂, m.p. 232°, [α]_D²⁰ -13.2°. The keto-acetate with Na-EtOH yields a dihydric alcohol, C₃₀H₅₂O₂, m.p. 258° (diacetate, m.p. 238—239°), also obtained from (II) and H₂O₂. It is inferred that (I) contains a bridge ring in the neighbourhood of the ethenoid linking and thus is not a derivative of hypocypene. Dehydrogenation of (I) gives 1:2:5-C₁₀H₅Me₃ and a solid hydrocarbon (1:2:5:6-C₁₀H₄Me₄?). F. R. S.

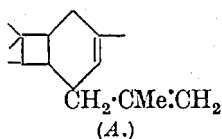
Polyterpenes and polyterpenoids. CXXV. Transformations and cyclisations of sclareol and dihydrosclareol. L. RŮŽICKÁ, L. LENGEL, and W. H. FISCHER [with M. FÜRTER] (Helv. Chim. Acta, 1938, 21, 364—370).—Sclareol (I) is converted by prolonged boiling with Ac₂O into the dicyclic doubly unsaturated primary alcohol (II), b.p. 140°/0.1 mm.,



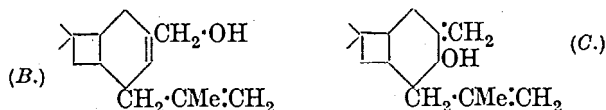
purified through the H phthalate. The corresponding acetate, b.p. 170—173°/0.3 mm., is cyclised by 90% HCO₂H to the tricyclic alcohol (III), b.p. 152°/0.9 mm., and cyclosclarene, b.p. 118—120°/0.2 mm. Dihydrosclareol (IV) is transformed by KHSO₄ at 120—125° and then at 130—140° into dihydrocyclosclarene, b.p. 142—145°/0.5 mm., dehydrogenated by Se at 340—360° to 1:7-di-, m.p. 130—131°, and 1:7:8-tri-, m.p. 144—145°, -methylphenanthrene, mainly the last-named. The product is not, however, homogeneous since it also contains 1:5:6-C₁₀H₅Me₃ also obtained by dehydrogenation of (I) and indicative of the presence of dicyclic constituents. The formation of small amounts of a non-cryst. hydrocarbon, C₁₈H₁₈ [picrate, m.p. 171—172°; additive compound with C₆H₅(NO₂)₃, m.p. 143—144°], is unexplained. The mol. refraction of (I) and (IV) is recorded. H. W.

Betulenols. II. Proof of the identity of betulenolic acid with homocaryophyllenic acid. W. TREIBS (Ber., 1938, 71, [B], 612—620).—The sesquiterpene alcohol from birch-bud oil, the sesquiterpene, C₁₅H₂₂, and the acid C₁₀H₁₆O₄ (A., 1936, 339) are re-named betulenol, betulenene, and betulenolic acid (I), respectively. Treatment of birch-bud oil with an amount of *o*-C₆H₄(CO)₂O insufficient for reaction with all the alcohols causes union first with α -betulenol (II), b.p. 154—156°/20 mm., α_D -19.5°,

and then with β -betulenol (III), b.p. 155—157°/20 mm., α_D -36°, whereas γ -betulenol (IV), b.p. 157—158°/20 mm., α_D -19.5°, remains unattacked. HCO_2H resinifies (IV), which is transformed by distillation with H_3BO_3 into H_2O and betulenes (V), $\text{C}_{15}\text{H}_{22}$, b.p. 132—135°/20 mm., α_D -11.5°, described previously as a component of birch-bud oil but not present in the oil and produced by dehydration of (IV). As a trebly unsaturated hydrocarbon (V) undergoes polymerisation when kept in COMe_2 to the substance, $(\text{C}_{15}\text{H}_{22})_n$, m.p. 220° after softening at 160°. The first runnings of the oil contain considerable amounts of C_{10}H_8 . Powerful oxidative degradation of (II), (III), and (IV) gives (I), which does not contain a *tert.* CO_2H since its Me_2 ester is readily and completely hydrolysed by boiling 0.1N-KOH-EtOH. The ester is converted by MgMeI into a *tetramethylglycol*, m.p. 103—104°, readily transformed by SOCl_2 into a substance, $\text{C}_{14}\text{H}_{26}\text{O}$, b.p. 112—117°/20 mm. More drastic oxidation of the glycol and its dehydration product affords $\alpha\alpha\alpha'\alpha'$ -tetramethylglutaric acid (VI), m.p. 186° (anhydride, m.p. 88°). The reactions of (I) resemble closely those of caryophyllenic acid and (I) is shown to be identical with a natural homocaryophyllenic acid of Ramage *et al.* (A., 1936, 994) but not with a synthetic acid of these workers (A., 1937, II, 109). The C skeleton (A) can without difficulty be assigned to (II). The acid mixture derived



by the oxidation of (III) with KMnO_4 is converted by hot $\text{MeOH-H}_2\text{SO}_4$ into a compound, $\text{C}_{11}\text{H}_{18}\text{O}_3$, b.p. 140—150°/20 mm., α_D +44.4°. This is transformed by MgMeI into a *dimethylglycerol*, $\text{C}_{13}\text{H}_{26}\text{O}$, m.p. 50°, and is therefore the lactone of a monocyclic dihydroxycarboxylic acid, $\text{C}_{11}\text{H}_{20}\text{O}_4$, rapidly degraded by HNO_3 to (I). It is



oxidised to (VI). The structures (B) and (C) are suggested provisionally for (III). (IV) and (V) are present in birch-bud oil in only very small amount and their position in the caryophyllene group depends at present on their behaviour when powerfully oxidised. (V) is a mixture of sesquiterpenes since it can be separated by MeOH into fractions of differing solubility and optical activity; their physical consts. and degradation indicate a close relationship to the caryophyllenes. H. W.

Decomposition products of lignin.—See A., 1938, III, 452.

Constituents of the leaves of certain *Leucadendron* species. I. *Leucodrin*. W. S. RAPSON (J.C.S., 1938, 282—286).—*Leucodrin* (I), m.p. 212—212.5°, has been isolated from the leaves of *L. concinnum*, *L. adscendens*, and *L. Stokoei*; rutin has also been obtained. (I) is a dilactone, $\text{C}_{15}\text{H}_{16}\text{O}_8$, containing one phenolic and three alcoholic OH; the phenolic OH is present in a $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_2\cdot\text{C}$ group. COMe_2 , HCl , and (I) give *isopropylideneleucodrin*, m.p. 229.5—231.5°, which yields a Ac_2 deriv-

ative, m.p. 168—169°. NH_3 , NH_2Et , and $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ with (I) afford respectively the *dihydroxy-diamide*, m.p. 175—176°, *bisethylamide*, m.p. 184—185°, and *bisbenzylamide*, m.p. 212°. *Tetra-acetyl-leucodrin*, m.p. 191—192°, is obtained from (I) and Ac_2O . CH_2N_2 and (I) form *leucodrin Me ether* (+ H_2O), m.p. 174—175°, oxidised (KMnO_4) to anisic acid, and converted into *isopropylideneleucodrin Me ether*, m.p. 161.5—162.5° (Ac derivative, m.p. 160.5—161.5°). The *Me ether* with Br yields *bromoleucodrin Me ether*, m.p. 243—244°, forming a CMe_2 derivative, m.p. 108—110°. (I) is extremely stable to the action of acids and alkalis. *Dibromoleucodrin*, m.p. 254—255°, obtained from (I) and Br , gives Ac_4 , m.p. 195—196°, and *tetrapropionyl* derivatives, m.p. 106—108°. *Dichloroleucodrin*, m.p. 236.5—239° (Ac_4 derivative, m.p. 171—172°), is similarly obtained; the halogen compounds are dilactones containing one acidic group and three reactive H. HNO_3 and (I) give a *dinitro-leucodrin*, m.p. 251° (decomp.). F. R. S.

Constituents of *Didymo-carpus pedicellata*.

I. **Isolation of a new series of colouring matters.** S. SIDDIQUI (J. Indian Chem. Soc., 1937, 14, 703—708).—The following cryst. products have been isolated, the yields being based on air-dried leaves: *pedicin*, $\text{C}_{14}\text{H}_7(\text{CO})(\text{OMe})_3(\text{OH})_2$, m.p. 145° (1.0%); *phenylhydrazone*, m.p. 165—167°; Bz_2 derivative, m.p. 181—183°; reduction product, $\text{C}_{18}\text{H}_{22}\text{O}_6$, m.p. 211°, *isopedicin*, $\text{C}_{18}\text{H}_{18}\text{O}_6$, m.p. 105° (0.4%), *pedicinin*, $\text{C}_{15}\text{H}_8\text{O}_4(\text{OH})\cdot\text{OMe}$, m.p. 203° (0.3%); NH_4 salt, m.p. 149°; *Ba salt*; Ac derivative, m.p. 175°, and *pedicellin*, $\text{C}_{15}\text{H}_7\text{O}(\text{OMe})_5$, m.p. 98° (1%). F. R. S.

Bitter principles of the columbo root. VI.

K. FEIST and W. VÖLKSEN (Annalen, 1938, 534, 41—56; cf. A., 1936, 1261).—The formation of COMe_2 by the action of KOH on chasmanthin (I) is probably due to the presence of CMe_2 since COMe_2 is not obtained from hexahydrochasmanthic acid or from merochasmanthic acid (II) or its *Me ether* (III) obtained by oxidising (I) with KMnO_4 . *Columbin* (IV) after purification by the method of Wessely *et al.* (A., 1936, 1575), *isocolumbin* (V), and *decarboxy-columbin* (VI) do not yield COMe_2 , which is obtained from *palmarin* (VII) (*isochasmanthin*), m.p. 261° after softening at 250°, $[\alpha]_D^{20} +6.60^\circ$. Methylation of (IV) in alkaline solution yields several products, chiefly *isocolumbin Me ether* which obstinately retains a material containing less C. When sublimed in a vac. this product leaves a small amorphous residue and gives mainly *decarboxyisocolumbin Me ether*, m.p. 204°; this could not be prepared from *decarboxy-isocolumbin*, which contains only 0.74 active H (Tschugaev-Roth) and hence is probably not a normal OH-compound. Reduction (Pd) of (VI) yields octahydrodecarboxycolumbic acid, m.p. 186° (*Me ester*, m.p. 81°). Distillation of (I) with Zn dust gives 1:2:5- $\text{C}_{10}\text{H}_5\text{Me}_3$ and *o*-cresol, also obtained from (V) derived from highly purified (IV). Liquid NH_3 and (II) give substance I, m.p. 190° (decomp.) (*Me ether*, m.p. 238°), and substance II, m.p. 184° (decomp.) (*Me ether*, m.p. 238°); under similar conditions (I) gives mainly (VII). *Palmarin Me ether*, m.p. 255° after softening at 245°, $[\alpha]_D^{20} +39.6^\circ$, with alkaline KMnO_4 appears to give exclusively (III).

The presence of CMe in (II) is established by oxidation, so that (II) contains a decahydronaphthalene ring with substituents thus:

$C_{10}H_{10}O(CO_2H)(Me)(OH)(CH_2 \cdot CO \cdot O)$. The lactone group is probably not that which becomes opened during the hydrogenation of (I). The eighth O of (II) is probably present as a masked CO. Determination of C-Me in (V), (VI), and (VII) gives less conclusive results but probably indicates 1 Me. The constitution of (II) and (VII) is discussed. H. W.

Red pigment of root of the beet (*Beta vulgaris*).

I. Betanin. II. Determination of betanin. G. W. PUCHER, L. C. CURTIS, and H. B. VICKERY (J. Biol. Chem., 1938, 123, 61—70, 71—75; cf. A., 1937, II, 206).—I. The isolation of betanin (I), $C_{21}H_{23}O_{10}N_2Cl_3H_2O$, is described; the method depends on the fact that an acid-EtOH extract of the dried root when neutralised with LiOH gives a ppt. which contains most of the pigment. Physical and chemical properties are described. A solution containing 0.005 mg. per c.c. has p_H 5.2. (I) appears to be a glucoside of a substance related to the anthocyanidins. There is probably no aliphatic NH_2 , and evidence for an aromatic NH_2 is inconclusive. A ring N may be present.

II. The light transmission of an aq. extract of dry tissue to which is added succinic acid-borate buffer of p_H 5.2 is determined with filter S53 of a Zeiss spectrophotometer. The concn., in terms of the purified pigment, which has extinction coeff. of 0.398 at concn. of 0.005 mg. per c.c., is then calc.

J. N. A.

Constituents of "Senso." III. Deacetyl- ψ -bufotalinamide and its Hofmann rearrangement. H. KONDO and S. IKAHA (J. Pharm. Soc. Japan, 1934, 54, 120—136).—MeOH solutions of Me deacetyl- ψ -bufotalinate, ψ -bufotalin, or deacetyl- ψ -methylbufotalin with NH_3 yield deacetyl- ψ -bufotalinamide (I), m.p. 210—212° (decomp.). On the basis of the Hofmann degradation and other degradative reactions of (I) it is concluded that the double linking in ψ -bufotalin is $\alpha\beta$ to the lactone ring, while the $>C:CO \cdot COMe$ grouping is not associated with the latter (cf. A., 1936, 478, 1252). CH. ABS. (r)

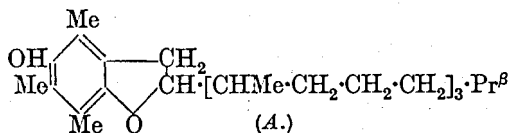
Chemical investigation of saponins. VII. Saponin from leaves of *Hedera japonica*, Tobler. S. KUWADA and T. MATSUKAWA (J. Pharm. Soc. Japan, 1934, 54, 13—25).—The sapogenin, $C_{30-31}H_{48-50}O_2$, m.p. 336—337° (many derivatives), appears to be identical with or closely related to α -hederagenin. CH. ABS. (r)

Absorption and fluorescence spectra of the colouring matters of litmus and red cabbage.—See A., 1938, I, 173.

Coumarones.—See B., 1938, 460.

Vitamin-E. P. KARRER, H. SALOMON, and H. FRITZSCHE (Helv. Chim. Acta, 1938, 21, 309—313).—The allophanates of neotocopherol from wheat-germ oil (Karrer *et al.*, A., 1938, II, 13), cumotocopherol (II) (John, A., 1937, III, 497), and β -tocopherol (Emerson *et al.*, A., 1938, II, 58) have the same m.p. and other properties and are alike in possessing vitamin-E action

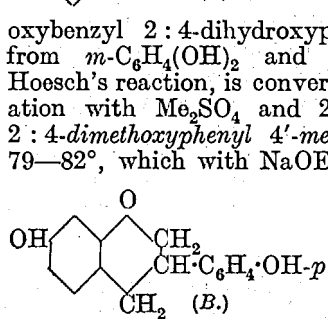
< that of α -tocopherol (II). When heated at 350° (II) gives duroquinol (Fernholz, A., 1937, II, 339) whereas (I) affords ψ -cumoquinol in small amount. It is unlikely that the tocopherols have the simple duro- or ψ -cumo-quinol ether structure for the following reasons. The allophanate (III), m.p. 176°, of duroquinol phytyl ether differs considerably from the allophanate (IV) of (II) in absorption spectrum and the product of its hydrolysis differs from (II) in this respect and in its inability to reduce $AgNO_3$. The allophanate, m.p. 178—180°, of duroquinol dihydrophytyl ether resembles (III) and the ether does not reduce $AgNO_3$. Exhaustive oxidation of (II) with $AgNO_3$ yields, not duroquinol, but one or more substances retaining all or nearly all the C atoms of (II). Active H cannot be detected and vitamin-E action is not pronounced. It appears therefore that the duroquinol portion and the hydrocarbon residue in (II) are united by C as well as by O linkings. (IV) is slowly transformed by $AcOH-HI$ at 150° into a hydrocarbon containing C and H in the ratio in which they are present in (II). Fission into a duren derivative and a fatty or monocyclic hydrocarbon does not occur. The structure (A) is therefore



suggested for (II). It is supported by the observations that 5-hydroxy-2-methylcoumaran strongly reduces $AgNO_3$ and greatly resembles (II) in absorption spectrum. H. W.

Constitution of equol. F. WESSELY, H. HIRSCHHEL, and G. SCHLÖGL-PETZIWAL [with F. PHILLINGER] (Monatsh., 1938, 71, 215—228; cf. Marrian *et al.*, A., 1935, 1032).—Equol (I), $C_{15}H_{14}O_3$, m.p. 192°, $[\alpha]_D^{20}$ -15.12° (Me_2 ester, m.p. 92° after prolonged softening; Ac_2 derivative, m.p. 128°), cannot be catalytically hydrogenated and is stable towards dil. acids. It gives $m-C_6H_4(OH)_2$ in good yield when dehydrogenated with Pd. When fused with KOH it gives $p-OH-C_6H_4-CO_2H$ and β -resorcylic acid which is shown to be a primary product of the change. Under somewhat different conditions molten KOH transforms (I) into β -4-hydroxyphenyl- α :2:4-dihydroxyphenyl- Δ^8 -propene (II), m.p. 162° after softening at 158° [Me_3 ether (III), m.p. 103.5° after softening at 99°; triacetate, m.p. 102° after softening at 98°, which gives a non-cryst. product (IV) when hydrogenated; tribenzoate, m.p. 182° after softening at 179°], hydrogenated to β -4-hydroxyphenyl- α :2:4-dihydroxyphenylpropane (V), m.p. 158° after softening at 156°, also obtained by hydrolysis of (IV). Ozonisation of (III) affords $p-C_6H_4Ac \cdot OMe$ and 2:4(OMe) $_2C_6H_3 \cdot CO_2H$. The "higher phenol" of Marrian (*loc. cit.*) contains 2 OH (not 3) and is not a primary product of the fission of (I) but is formed during the distillation of (II). If the latter is distilled repeatedly under diminished pressure it yields a glassy, non-cryst. distillate which gives a Bz_2 derivative, $C_{29}H_{24}O_5$, m.p. 136° after softening at 131°, and a Me_2 ether, $C_{17}H_{18}O_3$, m.p. 74° after softening at 66°, identical with the

compounds described by Marrian. Since these compounds are optically inactive and do not contain a double linking the fundamental phenol must be (A). 4'-Hydroxybenzyl 2:4-dihydroxyphenyl ketone, obtained from $m\text{-C}_6\text{H}_4(\text{OH})_2$ and $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$ by Hoesch's reaction, is converted by energetic methylation with Me_2SO_4 and 25% NaOH at 50° into 2:4-dimethoxyphenyl 4'-methoxybenzyl ketone, m.p. $79\text{--}82^\circ$, which with NaOEt and MeI affords 2:4-dimethoxyphenyl α -4'-methoxyphenylethylketone (VI). This is reduced by $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH to 2:4-dimethoxyphenyl- α -4'-methoxyphenylethylcarbinol transformed by $\text{K}_2\text{S}_2\text{O}_7$ at 180° into (II). Reduction of (VI) by Zn-Hg and conc. HCl affords (V). Hence (I) is (A) or (B). The absorption spectrum of (I) closely resembles that of œstrone but there appears otherwise no close chemical relationship. H. W.



Usnic acid. VI. Synthesis of *O*-dimethylpyrouric acid. H. F. BIRCH and A. ROBERTSON (J.C.S., 1938, 306—309).—Phloroglucinol Me_2 ether and $\text{CH}_2\text{Cl}\cdot\text{COMe}$ give 3:5-dimethoxyphenoxyacetone, b.p. $127\text{--}132^\circ/0.1\text{ mm.}$ (2:4-dinitrophenylhydrazones, m.p. 152°), cyclised to 4:6-dimethoxy-2-formyl-3-methylcoumarone, which with HCl-HCN forms the aldehyde, m.p. 155° (2:4-dinitrophenylhydrazones, m.p. 274°), identified by oxidation to the acid. The aldehyde, hippuric acid, and NaOAc yield 4:6-dimethoxy-3-methylcoumarone-2-pyruvic acid, m.p. $213\text{--}214^\circ$ (decomp.) [oxime, m.p. 153° (decomp.)], isolated through the azlactone, m.p. 183.5° ; the acid is converted by H_2O_2 into the corresponding 2-acetic acid, m.p. 148° . The acetate, m.p. 78.5° , of *C*-methylphloroglucinol $\beta\text{-Me}_2$ ether is isomerised ($\text{AlCl}_3\text{-PhNO}_2$) to 2-hydroxy-4:6-dimethoxy-5-methylacetophenone, b.p. $110\text{--}112^\circ/0.2\text{ mm.}$ (2:4-dinitrophenylhydrazones, m.p. $205\text{--}206^\circ$), which with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ gives *Et* 4:6-dimethoxy-3:5-dimethylcoumarone-2-carboxylate, m.p. 110° , hydrolysed to the acid, m.p. $219\text{--}220^\circ$ (decomp.). 4:6-Dimethoxy-3:5-dimethylcoumarone, prepared from 3:5-dimethoxy-4-methylphenoxyacetone (2:4-dinitrophenylhydrazones, m.p. 198°), forms 4:6-dimethoxy-2-formyl-3:5-dimethylcoumarone, m.p. 127° (2:4-dinitrophenylhydrazones, m.p. 252°), the constitution of which is proved by its oxidation to the corresponding acid. The aldehyde, hippuric acid, and NaOAc afford the azlactone, m.p. 205° , hydrolysed to 4:6-dimethoxy-3:5-dimethylcoumarone-2-pyruvic acid ($+\text{H}_2\text{O}$), m.p. 190° (decomp.), which is oxidised (H_2O_2) to the 2-acetic acid, identical with *O*-dimethylpyrouric acid. This synthesis confirms the constitution of pyrouric acid, usnetic acid, and decarbousnic acid. F. R. S.

Fixation of the aromatic ethylenic linkings in the coumarin ring system. S. RANGASWAMI and T. R. SESHADRI (Proc. Indian Acad. Sci., 1938, 7, A, 8—12).—Whereas the ethylenic linkings of coumarins are normally fixed so that one is internuclear, the alternative arrangement is also permissible as is shown

by the reactivity of 7-hydroxy-4:8-dimethylcoumarin (I) at position 6 in the following reactions. The *Ac* derivative, m.p. $135\text{--}136^\circ$; of (I) with AlCl_3 at 160° gives 7-hydroxy-6-acetyl-4:8-dimethylcoumarin, m.p. $192\text{--}193^\circ$. $\text{Hg}(\text{OAc})_2$, (I), and a little AcOH in MeOH give 7-hydroxy-4-methoxy-4:8-dimethyl-3:6-diacetoxymercuri-3:4-dihydrocoumarin, decomp. $>260^\circ$, converted by Br-AcOH into 3:6-dibromo-7-hydroxy-4:8-dimethylcoumarin, m.p. $>300^\circ$. $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ couples with (I) in AcOH-NaOAc . The 7-allyl ether (prep. by $\text{CH}_2\text{CH}\cdot\text{CH}_2\text{Br}$ and anhyd. K_2CO_3 in COMe_2), m.p. 108° , of (I) at $220\text{--}230^\circ$ gives 7-hydroxy-4:8-dimethyl-6-allylcoumarin, m.p. $168\text{--}170^\circ$. R. S. C.

Pechmann's condensation of methyl β -resorcylicate and β -resorcylic acid with ethyl acetoacetate. R. C. SHAH, S. M. SETHNA, B. C. BANERJEE, and D. CHAKRAVARTI (J. Indian Chem. Soc., 1937, 14, 717—720).—*Me* β -resorcylicate and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ with H_2SO_4 give *Me* 7-hydroxy-4-methylcoumarin-6-carboxylate, m.p. $212\text{--}214^\circ$ (*Ac*, m.p. $171\text{--}173^\circ$, and *Bz* derivatives, m.p. $173\text{--}174^\circ$; *Me* ether, m.p. $186\text{--}188^\circ$), and the corresponding acid, m.p. $284\text{--}285^\circ$, also obtained from β -resorcylic acid (I) and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$. Less efficient condensing agents are POCl_3 , P_2O_5 , and HCl . Malic acid and (I) yield 7-hydroxycoumarin-6-carboxylic acid, m.p. $268\text{--}269^\circ$ (lit. $244\text{--}260^\circ$). F. R. S.

Coumarins from phenols and acetoacetic esters. Constitution of halogenated resorcinols and orcinols. D. CHAKRAVARTI and S. M. MUKERJEE (J. Indian Chem. Soc., 1937, 14, 725—732).—4-Bromoresorcinol and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ give 6-bromo-7-hydroxy-4-methylcoumarin (I), m.p. 278° (*Ac* derivative, m.p. 170°), whilst the 3:4-*Me*₂, m.p. 275° (*Ac* derivative, m.p. 162°), and 4-methyl-3-ethyl compounds, m.p. 240° (*Ac* derivative, m.p. 152°), are obtained from $\text{CHMeAc}\cdot\text{CO}_2\text{Et}$ and $\text{CHEtAc}\cdot\text{CO}_2\text{Et}$, respectively. 4-Methylumbelliferone-8-diazoanhydride and CuBr-HBr yield 8-bromo-4-methylumbelliferone, m.p. $251\text{--}252^\circ$, and β -methylumbelliferone *Me* ether-6-diazobromide with CuBr-HBr affords 6-bromo- β -methylumbelliferone *Me* ether, m.p. 245° , also obtained from (I) and Me_2SO_4 . 2-Chloro-orscinol, m.p. 104° , from orcinol and SO_2Cl_2 , with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ gives 6-chloro-5-hydroxy-4:7-dimethylcoumarin, m.p. 264° (*Ac* derivative, m.p. 167°); the 3:4:7-*Me*₃, m.p. 276° (*Ac* derivative, m.p. 182°), and 4:7-dimethyl-3-ethyl compounds, m.p. 210° (*Ac* derivative, m.p. 173°), are similarly prepared. 6-Chloro-5-hydroxy-7-methylcoumarin-4-acetic acid, m.p. $275\text{--}280^\circ$ (lactone), is obtained from the chloro-orscinol and citric acid. 2-Bromo-orscinol, m.p. 142° , similarly gives 6-bromo-5-hydroxy-4:7-dimethyl-, m.p. 217° (*Ac* derivative, m.p. 197°), and -3:4:7-trimethyl-coumarin, m.p. 195° (*Ac* derivative, m.p. $158\text{--}159^\circ$). F. R. S.

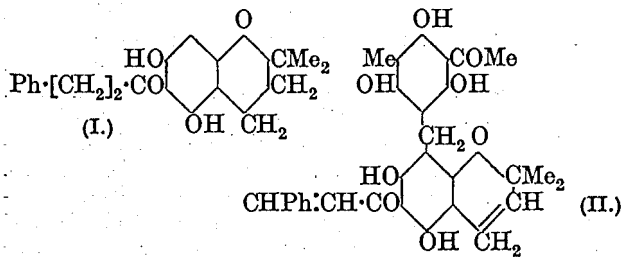
Heterocyclic compounds. VI. Coumarins from ethyl β -chloropropylacetoacetate and the mercuriation of coumarins from ethyl cyclohexanone-2-carboxylate. S. Z. AHMAD and R. D. DESAI (J. Univ. Bombay, 1937, 6, Part II, 89—92).—Allylacetoacetic ester, pyrogallol, and HCl give 7:8-dihydroxy-4-methyl-3- β -chloropropylcoumarin, m.p. $193\text{--}194^\circ$, converted into the -3-allylcoumarin

(cf. A., 1929, 574); phloroglucinol (I) affords 5:7-dihydroxy-4-methyl-3- β -chloropropylcoumarin, m.p. 198—199° (decomp.); orcinol (II) yields 5-hydroxy-4:7-dimethyl-3- β -chloropropylcoumarin, m.p. 206°; and α -C₁₀H₇·OH leads to 4-methyl-3- β -chloropropyl-5:6- α -naphtho-1:2-pyrone, m.p. 128°. Et cyclohexanone-2-carboxylate condenses with resorcinol, (I), (II), and 4-ethylresorcinol to give respectively 7-hydroxy- (? : 6 : 8-triacetoxymercuri-derivative), 5:7-dihydroxy-, m.p. 258° (6 : 8 : ?-triacetoxymercuri-derivative), 5-hydroxy-7-methyl-, m.p. 242—243° (6 : 8 : ?-triacetoxymercuri-derivative), and 6-ethyl-7-hydroxy-cyclohexeno-(1' : 2' : 4 : 3)-coumarin, m.p. 218°. F. R. S.

Flavone derivatives from glycerol ethers of resacetophenone. D. R. NADKARNI and T. S. WHEELER (J. Univ. Bombay, 1937, 6, Part II, 107—111).—2-Hydroxy-4-(β -dihydroxypropoxy)acetophenone with PhCHO, *p*-anisaldehyde, and salicylaldehyde gives 2-hydroxy-4-(β -dihydroxypropoxy)phenyl styryl ketone (I), m.p. 120°, 4-methoxystyryl ketone (II), m.p. 153°, and 2-hydroxystyryl ketone, m.p. 182°, respectively. (I) and SeO₂ form 7-(β -dihydroxypropoxy)flavone (+2H₂O), m.p. 87—88°, depropylated to 7-hydroxyflavone; similarly (II) yields 4'-methoxy-7-(β -dihydroxypropoxy)flavone (+3H₂O), m.p. 92—94°. Oxidation (H₂O₂) of (I) affords 7-(β -dihydroxypropoxy)flavonol, m.p. 153—155°, and (II) similarly gives the 4'-OMe-compound, m.p. 195°. Br and (I) yield 5-bromo-2-hydroxy-4-(β -dihydroxypropoxy)phenyl $\alpha\beta$ -dibromo- β -phenylethyl ketone, m.p. 200°, hydrolysed to 6-bromo-7-(β -dihydroxypropoxy)flavone, m.p. 156—157°, and the 4-OMe-compound, m.p. 116—117°, is obtained from (II). $\alpha\gamma$ -Bis-(3-hydroxy-4-acetylphenyl) ether and PhCHO give glycerol $\alpha\gamma$ -bis-(3-hydroxy-4-benzylideneacetylphenyl) ether, m.p. 210°, and the -4-*p*-anisylidene compound, m.p. 200—201°, is obtained from *p*-anisaldehyde. F. R. S.

Rottlerin. III. K. S. NARANG, J. N. RAY, and B. S. ROY (Current Sci., 1938, 6, 333; cf. A., 1938, II, 151).—The oxidation product (H₂O₂) of rottlerin Me₅ ether has m.p. 128°. With NaNO₂ in either AcOH or PrCO₂H, the same product, C₃₆H₄₀O₁₁N₂, m.p. 207° (decomp.), is obtained, and could not be derived by fixation of AcOH but by addition of N₂O₃. Tetrahydrorottlerin has mol. wt. 507 (C₃₁H₃₄O₈ requires 534) and the Me₅ ether, 572 (requires 600). F. R. S.

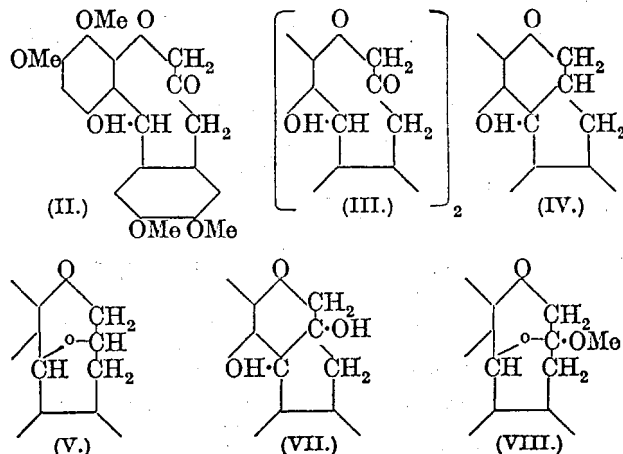
Rottlerin. II. A. MCGOOKIN, A. B. PERCIVAL, and A. ROBERTSON (J.C.S., 1938, 309—312; cf. A., 1937, II, 300).—Tetrahydrorottlerone (I) is C₂₀H₂₂O₄ and its Ac and Me derivatives are respectively



C₂₀H₂₀O₄Ac₂ and C₂₀H₂₀O₂(OMe)₂. The prep. of perhydrorottlerone from rottlerin (II) and (I) has

been reinvestigated; the compound has m.p. 147° and not 178° as previously stated. The constitutions (I) and (II) are suggested. F. R. S.

Brasilin and hæmatoxylin. XVI. Reduction products of tetramethylhæmatoxylone and trimethylbrasilone. P. PFEIFFER, E. DÖRING, H. KOBBS, and H. WERNER (J. pr. Chem., 1938, [ii], 150, 199—249).—Addition of Mg turnings to tetramethylhæmatoxylone (I) in AcOH-C₆H₆ at 30° gives tetramethylhæmatoxylonol (II), C₂₀H₂₂O₇, m.p. 188°, the pinacone (III), C₄₀H₄₂O₁₄, m.p. 287°, and 1.5—2% of α -tetramethylisohæmatoxylin (IV), C₂₀H₂₂O₆, α -, m.p. 196°, and β -form, m.p. 163°. 3% Na-Hg in AcOH-EtOH at 60° gives tetramethylallohæmatoxylin (V), C₂₀H₂₂O₆, α -, m.p. 166°, and β -form, m.p. 150°, and (II). Zn-Hg in hot AcOH-HCl gives 5% of tetramethyldeoxyhæmatoxylin (VI) and amorphous products. Zn dust in EtOH-AcOH at room temp. gives (III), (II), and μ' -hydroxytetramethylhæmatoxylin (VII), C₂₀H₂₂O₇, m.p. 194° (sinters at 192°). Structures shown are proved by the following reactions. (II)



gives a red-violet colour in H₂SO₄, contains 1 active H, gives a readily hydrolysed oxime, m.p. 206—208° (decomp.) (red-lilac in H₂SO₄), and an Ac derivative, m.p. 145—146° (no active H). With Me₂SO₄-KOH it gives a readily hydrolysed Me ether, m.p. 170° (red colour in H₂SO₄; no active H), which, since it gives no oxime, is probably (VIII). CrO₃ converts (VIII) into a substance, C₂₁H₂₂O₈, m.p. 207—208.5°. CrO₃ oxidises (II) to dihydrohæmatoxylinolactone (Me ester, m.p. 159—160°). Br-AcOH and (I) in light give a Br-derivative, m.p. 188°, oxidised by CrO₃ at >30° to bromotetramethylhæmatoxylone, m.p. 165—197° (loss of H₂O), which is similarly reduced by Mg to bromotetramethylhæmatoxylonol, m.p. 188°. H₂SO₄ dissolves (VII) to a red solution, which gradually becomes yellow (green fluorescence) owing to pyrylium sulphate formation. Alkali has no effect on (VII); CrO₃ in hot AcOH oxidises it to (I). With COMe₂ it gives an isopropylidene derivative, m.p. 157°, and is thus a *cis*-compound. Acylation gave only tars. Reduction by Na₂S₂O₄-HCl-EtOH or Zn dust in HCl-AcOH or in Ac₂O causes also loss of H₂O, giving mainly tetramethylanhydrohæmatoxylin (IX). H₂-Pd in AcOH gives (VI). The carbenium chloride, +0.5H₂O, and anhyd., bromide, and unstable iodide,

hydrolysed by H_2O , the *perchlorate* (almost stable to 10% NH_3), and *H sulphate* (hydrolysed by 10% NH_3) of (VII) are described. Treatment with hot KOH and a little EtOH, followed by MeI, gives the μ -*Me ether*, m.p. 147° (sinters at 144°) (carbenium chloride, $+2\text{H}_2\text{O}$, acid chlorides of varying composition, bromide, $+3\text{H}_2\text{O}$ and $+ \text{H}_2\text{O}$, and *perchlorate*, readily hydrolysed), which only slowly gives pyrylium salts and is oxidised by CrO_3 to (I) and reduced by $\text{Na}_2\text{S}_2\text{O}_4$ to (IX) or by H_2 -Pd to (VI). The chloride of (VII) with hot KOH-MeOH gives the μ' -*Me*, m.p. 159° (*perchlorate*; red colour in mineral acids), and with KOH-EtOH or NH_3 -EtOH the μ' -*Et ether*, m.p. 158° (*perchlorate*), both oxidised to (I) and hydrogenated to (VI). (IV) gives a red colour in H_2SO_4 , a stable *perchlorate*, but no Ac derivative, contains 1 active H, and is converted by P_2O_5 in hot C_6H_6 into a β -isomeride, m.p. 163° (Ac derivative, m.p. 144°), which, as is (IV), is converted by CrO_3 into a compound (? X), $\text{C}_{20}\text{H}_{20}\text{O}_7$, m.p. 172° (red colour in H_2SO_4 ; no CO derivatives). The β -form of (V) with P_2O_5 - C_6H_6 gives the α -form, which gives *solates*, m.p. about 125—135°, with 0.5EtOH, C_6H_6 , CHCl_3 , Et_2O , COMe_2 , or $\text{C}_6\text{H}_5\text{N}$. No active H is present. Neither form gives an Ac derivative. H_2SO_4 gives a red solution. The structure follows by analogy with the brasilone series. The pinacone and its Ac_2 derivative, m.p. 291°, give green colours in H_2SO_4 ; the former with CrO_3 gives (I). α - and β -forms are *cis-trans* isomerides.

Trimethylbrasilone and Zn dust in EtOH-AcOH give only 16—17% of μ' -hydroxytrimethylbrasilone (XI), now m.p. 167—167.5°, and some of the pinacone. Oxidation of (XI) gives the diketone and reduction by H_2 -Pd or $\text{Na}_2\text{S}_2\text{O}_4$ gives only trimethylanhydrobrasilone (XII). The readily hydrolysed, red carbenium *perchlorate*, chloride, $+2\text{H}_2\text{O}$ (loses $2\text{H}_2\text{O}$ and CH_3Cl at 80°/vac.) and $+ \text{H}_2\text{O}$, bromide, $+0.5\text{H}_2\text{O}$, and *H sulphate* of (XI) are described. With conc. KOH-EtOH and MeI (XI) gives the glassy μ -*Me ether*, m.p. about 54—60° [red colour in H_2SO_4 ; slowly gives a pyrylium salt; *perchlorate*; bromide, $+0.5\text{HBr}$, $+2\text{H}_2\text{O}$; reduced to (XII)], the chloride, $+3\text{H}_2\text{O}$, of which by loss of HCl and reduction gives a mixture. R. S. C.

Syntheses in the 7-hydroxycoumarin series.

A. N. NESMEJANOV, A. F. VOMPE, T. S. ZAREVITSCH, and D. D. SMOLIN (J. Gen. Chem. Russ., 1937, 7, 2767—2773).—4-Methylumbelliferone (I) in AcOH and $(\text{CH}_2)_6\text{N}_4$ (5 hr. at 100°) yield 7-hydroxy-8-aldehydo-4-methylcoumarin (II), m.p. 178—179° (*phenylhydrazone*, m.p. 249—250°; *oxime*, m.p. 245—246°), the Na salt of which, heated with $\text{COMe}\cdot\text{CH}_2\text{Cl}$ (3.5 hr. at 100°), yields 2-acetyl-4'-methyl-7':8'-furocoumarin, m.p. 216—217° (*phenylhydrazone*, m.p. 229—230°); this is unaffected by heating with 20% NaOH or KOH, or with 50% $\text{Ba}(\text{OH})_2$ at the b.p. Under these conditions (I) is converted into resorcinol, and 6:7-dihydroxy-4-methylcoumarin gives 1:3:4- $\text{C}_6\text{H}_3(\text{OH})_3$, whilst 7-methoxy-, 7-allyloxy- (III), and 7-(γ -dimethylallyloxy)-4-methylcoumarin (IV), m.p. 86—87° [from (I) and α -bromo- γ -methyl- Δ^2 -butene]

are recovered unchanged. (IV) is converted into (I) by heating with H_2SO_4 in EtOH (7 hr. at the b.p.), under which conditions (III) is unaffected. The Na salt of (II) and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in EtOH (12 hr. at the b.p.) give Et O-(8-aldehydo-4-methyl-7-coumaryl)-glycollate, m.p. 173—174°, hydrolysed by 20% KOH to the corresponding acid, decomp. at 200—202°, and by 5% H_2SO_4 in EtOH to (II). R. T.

Poly-membered cyclic compounds. X. Dodecamethylene, tridecamethylene, and tetradecamethylene sulphide. A. MÜLLER and A. F. SCHÜTZ (Ber., 1938, 71, [B], 692—695).—Gradual addition of $\text{Br}\cdot[\text{CH}_2]_{14}\cdot\text{Br}$ and Na_2S in EtOH to boiling EtOH gives tetradecamethylene sulphide, $[\text{CH}_2]_{14}\text{S}$, m.p. 72.5° {compound $([\text{CH}_2]_{14}\text{S})_2\cdot 3\text{HgCl}_2$ }. Tridecamethylene sulphide, m.p. 66°, and dodecamethylene sulphide, m.p. 66—66.5°, are obtained similarly. Tetra-, penta-, and tetradeca-methylene sulphide with MeI in COMe_2 at 130° or 160—170° give SMe_2I and $\text{I}\cdot[\text{CH}_2]_n\cdot\text{I}$ ($n = 4, 5, \text{ or } 14$). α -Diphenoxymethyldecane has m.p. 89—89.5°. H. W.

Indigoid dyes. II. S. K. GUHA (J. Indian Chem. Soc., 1937, 14, 709—712).—By condensing 6-methyl-3-hydroxythionaphthen with glyoxal, PhCHO , $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, and $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, respectively, bis-2-(6-methyl)thionaphthenethyleneindigo, m.p. 300° (decomp.), benzylidene-, m.p. 134—135°, 4'-nitrobenzylidene-, m.p. 228—229°, and 4'-dimethylaminobenzylidene-2-(6-methyl)thionaphthen, m.p. 193°, are obtained. 2:3-Naphthoxythiophen and the substituted acenaphthenequinone give 2:3-naphthathiophen-8'-(3'-chloro)-, -8'-(3'-bromo)-, and -8'-(1'-methoxy)-acenaphthyleneindigo, respectively. The properties of the dyes are described. F. R. S.

Spectrochemistry of pyridine derivatives. K. VON AUWERS (J. pr. Chem., 1938, [ii], 150, 166—172).—The substances of Graf and Langer (see following abstract) are excellent examples of the rules that alkyl substituents increase the dispersion and decrease the depression of n of $\text{C}_5\text{H}_5\text{N}$, particularly when an ethylenic linking is conjugated with the ring. CCl_3 is unusually effective in increasing n . 8-Azacoumarin has the anticipated n and dispersion. R. S. C.

Bases, $\text{C}_{10}\text{H}_{13}\text{N}$, [obtained] from paraldehyde and ammonia in the presence of ammonium acetate. R. GRAF and W. LANGER (J. pr. Chem., 1938, [ii], 150, 153—165).—Paraldehyde, conc. aq. NH_3 , and NH_4OAc at 180° give much 2-methyl-5-ethylpyridine (I), smaller amounts of α - and γ -picoline and mixed bases, and much resin. Fractionation of the mixed bases and purification by way of the picrates gives 2-methyl-5- Δ^2 -n-butenylpyridine (II), b.p. 94°/12 mm. (oily platinichloride; picrate, m.p. 120—121°), with smaller amounts of β -collidine, 2-methyl-5-n- Δ^2 -n-butenyl- (III), b.p. 98—99°/12 mm. (picrate, m.p. 162°; platinichloride, m.p. 168—170°), and 3-ethyl-5-n-propylidene-pyridine (IV), b.p. 103—104°/12 mm. (picrate, m.p. 129°; platinichloride, m.p. 156—157°). These products arise by initial formation of hexatrienal (or an aldol) and $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ (or aldol), which condense with each other and NH_3 to (II). The function of the NH_4OAc is to catalyse self-condensation of the aldehyde. Isomerisation of (II)

gives (III) (effected also by long boiling with 50% H_2SO_4). Paraldehyde and (I) at 100° give much (IV), which accounts for the presence of (IV) in the main reaction. Structures are proved as follows. Oxidation of (IV) gives AcOH and 5-ethylpicolinic acid, and hydrogenation gives 5-ethyl-3-*n*-propylpyridine, b.p. about $90^\circ/13$ mm. (picrate, m.p. $99-100^\circ$). Hot aq. KMnO_4 oxidises (I) to isocinchomeronic acid; cold KMnO_4 or hot HNO_3 gives 6-methylnicotinic acid, also obtained with CO_2 and AcOH by $\text{CrO}_3-\text{H}_2\text{SO}_4$. Hydrogenation (Pd-C) in EtOH gives (2 H absorbed) 2-methyl-5-*n*-butylpyridine (V), b.p. $89^\circ/12$ mm. (platinichloride, m.p. $134-135^\circ$; picrate, m.p. $135-136^\circ$). 4 Br add smoothly to (II), but the product is oily. O_3 gives MeCHO and a substance yielding 6-methyl-5-pyridylacetaldehydephenylhydrazone (or 6-methylpyridylglyoxalosazone), m.p. $191-193^\circ$ (decomp.). CrO_3 yields EtCO_2H from (III). 5-Cyano-2-methylpyridine (hydrochloride, sublimes), prepared from the amide and POCl_3 at 130° , with MgPr^{I} gives 2-methyl-5-pyridyl Pr^{a} ketone, b.p. $126^\circ/12$ mm., hydrogenated (Pd-C) to α -2-methyl-5-pyridyl-*n*-butyl alcohol, b.p. $150-155^\circ/\text{vac.}$, which is dehydrated by P_2O_5 to (III). Hydrogenation of (III) yields (V). R. S. C.

Substituted imides of tetra-alkylsuccinic acids and their physiological action. E. OTT and F. HESS (Arch. Pharm., 1938, 276, 181-185).—Fusion of tetramethylsuccinic anhydride (I) with 2-aminopyridine yields N-2-pyridyltetramethylsuccinimide (II), b.p. $197^\circ/15$ mm., m.p. 85° , the structure of which is proved by synthesis from 2-chloropyridine and K tetramethylsuccinimide. Similarly are obtained N-2-pyridyl-*s*-dimethyldiethylsuccinimide, b.p. $207^\circ/10$ mm., N-2-pyridyltetraethylsuccinimide, (III), b.p. $189^\circ/0.1$ mm., m.p. 89° , and (from 2:6-diaminopyridine) N-(6-amino-2-pyridyl)tetraethylsuccinimide, b.p. $230^\circ/0.1$ mm., m.p. 118° . From α -aminonitroline α -nicotyltetraethylsuccinimide, b.p. $235^\circ/0.1$ mm., m.p. 105° (hydrochloride, m.p. 125°), is formed. With $\text{NEt}_2\text{[CH}_2\text{]}_2\text{NH}_2$ (I) yields N-(β -diethylaminoethyl)tetramethylsuccinimide (IV), b.p. $159^\circ/16$ mm., whilst $(\text{NH}_2\text{CH}_2\text{CMe}_2)_2$ gives N-(δ -amino- $\beta\beta\gamma$ -tetramethylbutyl)tetramethylsuccinimide (V), b.p. $180^\circ/15$ mm. (hydrochloride, m.p. 187°).

Tetraethyl- and tetramethyl-succinimide with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{K}$ yield respectively N-(carboxymethyl)-tetraethyl- (VI), m.p. 87° , and N-(carboxymethyl)tetramethylsuccinimide (VII), m.p. 90° . (II) and (III) are hypnotics, (IV) and (V) have analeptic action, and (VI) and (VII) have a caffeine-like action.

J. D. R.

Behaviour of quaternary pyridinium salts and quaternary salts of other cyclic bases towards sodium hyposulphite, $\text{Na}_2\text{S}_2\text{O}_4$. P. KARRER, F. W. KAHNT, R. EPSTEIN, W. JAFFE, and T. ISHII (Helv. Chim. Acta, 1938, 21, 223-236).—Attempted reduction of the methiodides of $\text{C}_5\text{H}_5\text{N}$, 2-methyl- and 2:6-dimethyl-pyridine with $\text{Na}_2\text{S}_2\text{O}_4$ in aq. NaHCO_3 gives yellow solutions from which the initial materials are recovered unchanged. Treatment of lauryl-, m.p. 92° , tetradecyl-, m.p. 85.5° , cetyl-, m.p. 83° , and octadecyl-, m.p. 82° , -pyridinium chloride with $\text{Na}_2\text{S}_2\text{O}_4$ in aq. NaHCO_3 or Na_2CO_3 gives soap-

like products which contain S and are regarded as formed by addition of $\text{Na}_2\text{S}_2\text{O}_4$ or NaHSO_3 to the primary 1-alkyl-*o*-dihydropyridines. Comparison with the 1-alkyl-*o*-dihydropyridines establishes the stabilising action of $m\text{-CO}\cdot\text{NH}_2$. A preliminary normal reduction is assumed from measurement of the CO_2 evolved thus: $\text{Na}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{NaHSO}_3$; $2\text{NaHSO}_3 + 2\text{NaHCO}_3 \rightarrow 2\text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O} + \text{CO}_2$; $\text{C}_5\text{H}_5\text{N}\cdot\text{RCl} + \text{H}_2 \rightarrow \text{HCl} + \text{C}_5\text{H}_5\text{NHR}$; $\text{HCl} + \text{NaHCO}_3 \rightarrow \text{NaCl} + \text{H}_2\text{CO}_3$; $\text{C}_5\text{H}_5\text{NHR} + \text{H}_2\text{CO}_3 \rightleftharpoons \text{C}_5\text{H}_5\text{NHR}\cdot\text{H}_2\text{CO}_3$. Compounds containing less S are obtained from Na amidoimidomethanesulphinate and 1-alkylpyridinium chlorides in presence of NH_3 . Substances free from S are derived by use of $\text{Na}_2\text{S}_2\text{O}_4$ and conc. NaOH; these are doubtless 1-alkyl-*o*-dihydropyridines but their purification is hindered by their great instability and small crystallising power. The influence of $m\text{-CO}\cdot\text{NH}_2$ on the rate of reduction of 1-alkylpyridinium salts is uncertain. The hydrochlorides of 1-lauryl-, 1-tetradecyl-, and 1-cetyl-piperidine have m.p. $188-189^\circ$, $186-187^\circ$ and 180° , respectively; cryst. 1-cetyl-piperidine is described. Attempts to reduce stilbazole methiodide, m.p. 220° , were unsuccessful. $\text{Na}_2\text{S}_2\text{O}_4$ rapidly converts quinoline methiodide or benzylidide, or isoquinoline methiodide or octidide, into strongly reducing, red or red-brown compounds which rapidly become completely resinified. The compounds from tetradecylisoquinolinium chloride and cetylisoquinolinium iodide contain 3.5-4% S; lauryl- and cetylisoquinolinium chlorides are described. isoQuinolinium compounds with a glucose residue yield better results. Thus isoquinoline and acetobromoglucose yield tetra-acetyl-d-glucosidoisoquinolinium bromide, m.p. 192° , transformed by $\text{Na}_2\text{S}_2\text{O}_4$ into a H_2 -derivative which strongly reduces AgNO_3 . 1-Tetra-acetylglucosido-2-methylpyridinium bromide, m.p. 172° , is obtained in very small yield but the corresponding compound with $\text{CO}\cdot\text{NH}_2$ at C_5 , could not be obtained. These compounds appear particularly valuable since their H_2 -derivatives must show different absorption spectra according to the manner in which the 2 H are added. The spectrum of sorbamide is recorded for purposes of comparison. isoNicotinamide methiodide, m.p. 255° , is not reduced by $\text{Na}_2\text{S}_2\text{O}_4$. 4:4'-Dipyridyl dimethiodide appears to be converted into the same violet reduction product by $\text{Na}_2\text{S}_2\text{O}_4$ as by other reducing agents; it is certainly not a normal $o\text{-H}_2$ -derivative. H. W.

1-Azadicyclo[1:2:2]heptane. G. R. CLEMO and V. PRELOG (J.C.S., 1938, 400).—4-Piperidyl-carbinol, P, and HI give 4-iodomethylpiperidine hydriodide, m.p. $132-133^\circ$, which with NaOH and PhSO_2Cl yields 1-azadicyclo[1:2:2]heptane, m.p. $78-79^\circ$. F. R. S.

Exchange of hydrogen atoms between pyrrole, indole, and their methyl derivatives and water.—See A., 1938, I, 255.

Action of sulphuryl chloride on quinoline oxide. B. BOBRAŃSKI (Ber., 1938, 71, [B], 578-582).—Treatment of quinoline oxide hydrochloride with SO_2Cl_2 gives 4- and 2- (I) (picrate, m.p. 122°) -chloroquinoline and tetrachloroquinoline, m.p. 158° . Cl is

retained so loosely in (I) that 2-hydroxyquinoline results when (I) is boiled with dil. HCl. H. W.

Sulphonamides. A. K. CHOUDHURY, P. DAS-GUPTA, and U. BASU (J. Indian Chem. Soc., 1937, 14, 733—735).—*p*-Acetamidobenzenesulphonyl chloride condenses with 8-aminoquinoline, 8-amino-6-methoxyquinoline, *p*-anisidine, δ -diethylaminobutylamine, and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ to give respectively 4-aminobenzenesulphon-8'-quinolylamide (I), m.p. 193° (Ac derivative, m.p. 192°), -6'-methoxy-8'-quinolylamide, m.p. 189° (Ac derivative, m.p. 222°), -4'-methoxyphenylamide, m.p. 195° (Ac derivative, m.p. 197°), and - δ -diethylaminobutylamide, hydrochloride (II), m.p. 172°, and 4-acetamidobenzenesulphon-4'-carbethoxyphenylamide, m.p. 220°. Examination of the bacteriostatic activity of (I) and (II) suggests that the replacement of the amido-H of $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ lowers the activity and increases the toxicity of the compound. F. R. S.

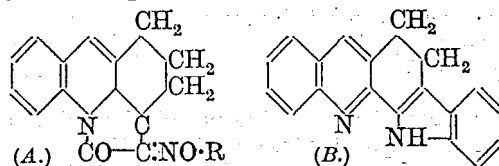
Transformation of α -ethoxycinchonic acid into ethyl α -hydroxycinchonate. H. KONDO and T. NOZOE (J. Pharm. Soc. Japan, 1936, 56, 10—16).—When heated, 2-ethoxycinchonic acid passes into an equilibrium mixture with Et 2-hydroxycinchonate and Et 2-ethoxycinchonate. CH. ABS. (r)

Synthesis of spasmolytically active 3-methylisoquinolines. V. BRUCKNER and G. VON FODOR (Ber., 1938, 71, [B], 541—549).—The acetate of the requisite β -amino- α -arylpropanol is hydrolysed with 10% H_2SO_4 at 100° and the resulting solution is neutralised and treated with the necessary acid chloride in C_6H_6 at about 40° in presence of alkali, thus giving β -*p*-anisoylamido-, m.p. 179°, β -veratroylamido-, m.p. 158°, and β -3 : 4 : 5-trimethoxybenzamido-, m.p. 119—120°, α -3 : 4-methylenedioxyphenylpropanol, β -phenylacetamido-, m.p. 116°, β -homoveratroylamido-, m.p. 142°, β -piperonylamido-, m.p. 156°, β -benzamido-, m.p. 136°, β -*p*-anisoylamido-, m.p. 137°, β -veratroylamido-, m.p. 156°, β -piperonylamido-, m.p. 148°, β -3 : 4 : 5-trimethoxybenzamido-, m.p. 159°, and β -3 : 4 : 5-triethoxybenzamido-, m.p. 75° (also + 1MeOH), α -3 : 4-dimethoxyphenylpropanol. Cyclisation of the amines by POCl_3 in PhMe or xylene (purification described) gives the following isoquinolines: 6 : 7-methylenedioxy-1-*p*-anisyl-3-methyl- [hydrochloride (+1H₂O), m.p. 180°]; 6 : 7-methylenedioxy-1-3' : 4'-dimethoxyphenyl-3-methyl-, m.p. 160—161°; 6 : 7-methylenedioxy-1-3' : 4' : 5'-trimethoxyphenyl-3-methyl-, m.p. 152—153°; 6 : 7-dimethoxy-1-phenyl-3-methyl-, m.p. 128° [hydrochloride, m.p. 245° (decomp.)]; 6 : 7-dimethoxy-1-*p*-anisyl-3-methyl- [hydrochloride, m.p. 185° (decomp.)]; 6 : 7-dimethoxy-1-3' : 4'-dimethoxyphenyl-3-methyl-, m.p. 143° (hydrochloride, m.p. 193°); 6 : 7-dimethoxy-1-3' : 4'-methylenedioxyphenyl-3-methyl-, m.p. 186° [hydrochloride, m.p. 190—191° (decomp.)]; 6 : 7-dimethoxy-1-3' : 4' : 5'-trimethoxyphenyl-3-methyl-, m.p. 186° (hydrochloride, m.p. 122°); 6 : 7-dimethoxy-1-3' : 4' : 5'-triethoxyphenyl-3-methyl-, m.p. 122° (hydrochloride, m.p. 201°); 6 : 7-dimethoxy-1-benzyl-3-methyl-, m.p. 106° [hydrochloride (+1H₂O), m.p. 204°]; 6 : 7-dimethoxy-1-3' : 4'-dimethoxybenzyl-3-methyl-, m.p. 136°; 6 : 7-dimethoxy-1-3' : 4'-methylenedioxybenzyl-3-methyl-, m.p. 129°. All the iso-

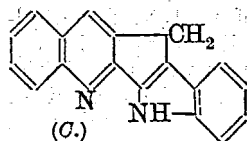
quinoline derivatives exhibit pharmacological action equal to or exceeding that of papaverine. H. W.

Carbazole derivatives.—See B., 1938, 356.

Condensation of tetrahydroacridine and 7-aza-5 : 6-benzohydrindene with ethyl oxalate. W. BORSCHKE and R. MANTEUFFEL (Annalen, 1938, 534, 56—67).—Tetrahydroacridine, KOEt, and $\text{Et}_2\text{C}_2\text{O}_4$ in Et_2O give Et 1 : 2 : 3 : 4-tetrahydroacridyl-1-glyoxylylate (I), m.p. 119° [oxime, m.p. 194—195° (decomp.)], the *K* compound of which is transformed by dil. AcOH at 0° into tetrahydroacridyl-1-glyoxylic acid, m.p. 188—189° (decomp.) [phenylhydrazone, m.p. 216° (decomp.)]. The corresponding oxime (II), m.p. 172—173° (decomp.), with Ac_2O or BzCl in $\text{C}_6\text{H}_5\text{N}$ gives anhydrides (cf. A), m.p. 180° and 168—169° (decomp.), respectively. Distillation of (II) under 1 mm. yields 1-cyanotetrahydroacridine (III), m.p. 99—100° (picrate, m.p. 174—175°), converted by boiling HCl-EtOH into Et tetrahydroacridine-1-carboxylate [picrate, m.p. 160—161° (decomp.)]; the corresponding free acid slowly loses CO_2 at room temp., yielding 1 : 2 : 3 : 4-



tetrahydroacridine (picrate, m.p. 220—221° after softening and darkening at 210°). Diazotised $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ and (III) afford 1-*p*-anisylazo-1-cyanotetrahydroacridine, m.p. 123° (decomp.); 1-*p*-bromobenzeneazo-1-cyanotetrahydroacridine, m.p. 154—155° (decomp.), is obtained similarly. Diazotised NH_2Ph and (I) in $\text{C}_6\text{H}_5\text{N}$ afford 1-ketotetrahydroacridinephenylhydrazone, m.p. 110°, converted by boiling EtOH saturated with HCl into 9-aza-1 : 2-[2' : 3'-(1'-azanaphtho)]-1 : 2 : 3 : 4-tetrahydrofluorene (B), m.p. 205—206° (hydrochloride, m.p. 300—301°; picrate, m.p. 254—255°). 4-Ketotetrahydroacridine-*p*-anisyl-, m.p. 163°, and -*p*-bromophenyl-hydrazone, m.p. 153°, and 6-bromo-9-aza-1 : 2-[2' : 3'-(1'-azanaphtho)]-1 : 2 : 3 : 4-tetrahydrofluorene, m.p. 216° (hydrochloride, decomp. about 350°), are described. Trimethylenequinoline, KOEt, and $\text{Et}_2\text{C}_2\text{O}_4$ in Et_2O yield Et 7-aza-5 : 6-benzohydrindyl-1-glyoxalate (IV), m.p. 171—172° [oxime, m.p. 225° (decomp.)], the *K* derivative of which is converted by boiling abs. EtOH followed by AcOH into 7-aza-5 : 6-benzohydrindyl-1-glyoxylic acid, m.p. 242—243° (decomp.). The oxime, m.p. 162—163°, is transformed by cautious distillation, less advantageously by acylation in $\text{C}_6\text{H}_5\text{N}$ followed by distillation, into 1-cyano-7-aza-5 : 6-benzohydrindene, m.p. 128—129° (picrate, m.p. 181—182°), which gives 1-cyano-1-*p*-bromobenzeneazo-7-aza-5 : 6-benzohydrindene, m.p. 175—176° (decomp.). With the requisite azo-compound (IV) yields 1-keto-7-aza-5 : 6-benzohydrindenephenylhydrazone, m.p. 170—173° after softening at 150° (transformed by crystallisation from C_6H_6 -light petroleum into a product, m.p. 113—114°), whence 4 : 12-diaza-2 : 3-benzodiphen-succindene (C), m.p. 257—259° (hydrochloride; picrate,



decomp. 257° after darkening at 254°), and 1-*keto*-7-*aza*-5 : 6-*benzohydrindene*-*p*-*bromophenylhydrazone*, m.p. 174—175°, whence 7-*bromo*-4 : 12-*diaza*-2 : 3-*benzodiphenysuccindene*, m.p. 300° [hydrochloride, m.p. >360°; picrate, m.p. 277° (decomp.)]. H. W.

Acridine derivatives. I. M. L. DEAR, K. S. NARANG, and J. N. RAY (J.C.S., 1938, 304—305).—*p*-Anisidine and 2-chloro-5-nitrobenzoic acid give 4-nitro-4'-methoxydiphenylamine-2-carboxylic acid, m.p. 225° (lit. 216—220°), cyclised to 5-chloro-3-nitro-7-methoxyacridine, m.p. 223° (lit. 220—221°). This substance with *p*-anisidine yields 3-nitro-5-*p*-anisidino-7-methoxyacridine (I), m.p. 212°, reduced to the 3-amino-derivative, m.p. 182° (decomp.) [Ac derivative, m.p. 258° (decomp.)] Condensation of (I) with other reagents leads to 3-nitro-, m.p. 181° [hydrochloride, m.p. 281° (decomp.)], and 3-amino-5-*p*-phenetidino- [hydrochloride, m.p. 280° (decomp.)]; Ac derivative, m.p. 235—237°, 3-nitro-5-piperidino-, m.p. 220° (decomp.), 3-nitro-, m.p. 270° (decomp.), and 3-amino-5-*p*-acetamidoanilino-, m.p. 279—280° (decomp.), and 3-nitro- (hydrochloride, m.p. 242°) and 3-acetamido-5-butylamino-7-methoxyacridine, m.p. 230° F. R. S.

Synthesis of 5 : 6 : 7 : 8-tetrahydrophenanthridine and its derivatives. J. KENNER, W. H. RITCHIE, and F. S. STATHAM (J.C.S., 1937, 1169—1172).—2-Hydroxymethylcyclohexanone (or the reaction mixture from CH₂O and cyclohexanone) with NH₂Ph and SnCl₄ gives 5 : 6 : 7 : 8-tetrahydrophenanthridine, m.p. 64° (picrate, m.p. 210—212°), dehydrogenated (Se) to phenanthridine [platinichloride, m.p. 219—221° (decomp.)]. By using substituted amines, the following have been obtained : 3-methyl-, m.p. 73·5° [picrate, m.p. 231—232° (decomp.)]; 3-methylphenanthridine, m.p. 89° (lit. 131°), and its picrate, m.p. 266° (decomp.) (lit. 202°), 1-methyl-, m.p. 80·5° [picrate, m.p. 203—204° (decomp.)]; 1-methylphenanthridine, m.p. 95·5° (lit. 70°), and its picrate, m.p. 234° (decomp.) (lit. 220°), 1 : 3-dimethyl-, m.p. 49·5—50·5° [picrate, m.p. 212·5° (decomp.)]; 1 : 3-dimethylphenanthridine, m.p. 84·5°, and its picrate, m.p. 261° (decomp.), 1 : 4-dimethyl-, m.p. 63—63·5° [picrate, m.p. 180—181° (decomp.)]; 1 : 4-dimethylphenanthridine, m.p. 76·5°, and its picrate, m.p. 222°, 3-bromo-, m.p. 110° [picrate, m.p. 221—222° (decomp.)], 3-chloro-, m.p. 90° [picrate, m.p. 214° (decomp.)], 1-nitro- [picrate, m.p. 216—217° (decomp.)], 3-methoxy-, m.p. 110—111° [picrate, m.p. 241—242° (decomp.)], 1 : 4-dimethoxy-, m.p. 86·5—87°, and 7-methyl-5 : 6 : 7 : 8-tetrahydrophenanthridine, m.p. 45° [picrate, m.p. 195—196° (decomp.)]; 7-methylphenanthridine, m.p. 88°, and its picrate, m.p. 236—237° (decomp.), and tetrahydro- α -naphthaphenanthridine, m.p. 118° [picrate, m.p. 215—216°]. The *p*-nitrophenylhydrazones of 4-methyl-2-hydroxymethylcyclohexanone, m.p. 144—145°, and 2-methylene- α -tetralone, m.p. 106—107°, are also described. F. R. S.

Phenanthridine series. V. Colour and antiseptic properties of quaternary salts. (SIR) G. T. MORGAN, and L. P. WALLS, with a note by C. H. BROWNING, Y. GULBRANSEN, and J. V. M. ROBB (J.C.S., 1938, 389—397).—By methylation of the corresponding compounds containing NH₂, the *dtert*.

amines, 3-dimethylamino-9-methyl- and 9-*p*-dimethylaminophenyl-phenanthridine, have been prepared, and from the latter the three possible quaternary salts have been obtained. Bases (primary and *tert*.) and Ac derivatives derived from 9-*p*-aminophenylphenanthridine are colourless or almost so, but monoacid salts and those with hetero-N alone quaternary are red. The appearance of colour is always associated with the possibility of valency tautomerism (involving electron displacements only) and thus is probably due to wave-mechanical resonance. The antiseptic properties of 31 compounds, including a series of NH₂-compounds derived from 9-chloro- and 9- ω -chloromethylphenanthridine, are reported, and some are shown to be powerfully active both in peptone water and in a serum medium.

The following are described : 3-amino-9-methylphenanthridine hydrochloride; 3-dimethylamino-9-methylphenanthridine, m.p. 146° (hydrochloride); 3-acetamido-9 : 10-dimethylphenanthridinium chloride (+H₂O) and iodide; 9-*p*-aminophenylphenanthridine hydrochloride; 9-*p*-dimethylaminophenylphenanthridine, m.p. 179—181° (hydrochloride); 9-*p*-aminophenyl-10-methylphenanthridinium iodide; 9-*p*-acetamidophenyl-10-methylphenanthridinium chloride (+2H₂O); 9-phenanthridyl-*p*-phenyltrimethylammonium iodide, m.p. 179° (decomp.), remelts 235°; 9-*p*-dimethylaminophenyl-10-methylphenanthridinium *p*-toluenesulphonate (+2H₂O), m.p. 120°, iodide, m.p. 238° (decomp.), and chloride di-iodide, m.p. 232—236° (decomp.); 5-nitro-2-*p*-nitrobenzamido-diphenyl, m.p. 209°, which with POCl₃ gives 3-nitro-9-*p*-nitrophenylphenanthridine, m.p. 294°, reduced to the 3-amino-9-*p*-amino-compound, m.p. 233° [hydrobromide; sulphate; Ac₂ derivative, m.p. 327—328° (decomp.)]; 3-acetamido-9-*p*-acetamidophenyl-10-methylphenanthridinium chloride; 3-amino-9-*p*-aminophenyl-10-methylphenanthridinium chloride (+5H₂O); 4'-nitro-2-*p*-nitrobenzamido-diphenyl, m.p. 208°; 7-nitro-9-*p*-nitrophenylphenanthridine, m.p. 327°, and the 7-amino-9-*p*-amino-compound, m.p. 212° (sulphate; Ac₂ derivative, m.p. 172—173°); 7-acetamido-9-*p*-acetamidophenyl-10-methylphenanthridinium *p*-toluenesulphonate and chloride (+1·5H₂O), m.p. 231° (decomp.); 7-amino-9-*p*-aminophenyl-10-methylphenanthridinium chloride (+0·5H₂O), m.p. 262° (decomp.); 4'-nitro-2-benzamidodiphenyl, m.p. 165·5°; 7-nitro-9-phenylphenanthridine, m.p. 237°; 5 : 4'-dinitro-2-benzamidodiphenyl, m.p. 250°; 3 : 7-dinitro-9-phenylphenanthridine, m.p. 275—277°; 9-methylaminophenanthridine, m.p. 187° [sulphate (+0·5H₂O); Ac derivative, m.p. 155°]; 9-dimethylaminophenanthridine, m.p. 61·5° (hydrochloride); 9-phenanthridyltrimethylammonium iodide, m.p. 234° (decomp.); 9-dimethylamino-10-methylphenanthridinium iodide, m.p. 230° (efferv.); 9- ω -phenanthridylmethyltrimethylammonium iodide, m.p. about 222° (decomp.); 9- ω -phenanthridylmethyl-N-pyridinium chloride, decomp. about 250°; and 9- ω -piperidino-methylphenanthridine, m.p. 90—93° [hydrochloride (+H₂O)]. F. R. S.

Thioformamides.—See B., 1938, 352.

α -Hydroxystyryl derivatives of pyridine, thiazoline, benzthiazole, and thiazole. Pyrazolones.—See B., 1938, 460.

2-Undecyl- and 2-heptadecenyl-glyoxaline.—See B., 1938, 354.

[New derivatives of pyrimidine.] W. HUBER and H. A. HÖLSCHER (Ber., 1938, 78, [B], 706; cf. A., 1938, II, 114).—An acknowledgment of the priority of Todd *et al.* (A., 1936, 1526) in the prep. of 2-amino-6-hydroxy-4-ethyl-, 6-chloro-2-amino-4-ethyl-, and 2:6-diamino-4-ethyl-pyrimidine. H. W.

Aminoindolizine derivatives. H. KONDO and T. NISHIZAWA (J. Pharm. Soc. Japan, 1936, 56, 1—6).—PhN₂Cl and 1-acetyl-2-methylindolizine (I) give 1-acetyl-2-methylindolizine-3-azobenzene, m.p. 77°. 3-Amino-1-acetyl-2-methylindolizine, m.p. 172° (from Na azobenzenesulphonate) (hydrochloride, m.p. 254°; Ac derivative, m.p. 219°), gives, with PhNCS, 1-acetyl-2-methyl-3-indolizine phenylurethane, m.p. >330°. With NaNO₂ in AcOH (I) yields 3-nitroso-1-acetyl-2-methylindolizine, m.p. 146.5° (decomp.).

CH. ABS. (r)

Diene synthesis in the indolizine series. H. KONDO and K. HAMAMOTO (J. Pharm. Soc. Japan, 1936, 56, 7—10).—Maleic anhydride (I) and 2-methylindolizine give an adduct, C₁₇H₁₇O₃N, m.p. 144° (decomp.), methylated (CH₃N₂) to a substance, C₂₁H₂₅O₃N, m.p. 126.5—127°, which is hydrogenated (Pd) to a compound, m.p. 127°. 1-Acetyl-2-methylindolizine and (I) give a compound, m.p. 191—192°.

CH. ABS. (r)

2-Hydroxy-3:4-dihydroquinoxaline.—See B., 1938, 460.

Synthesis of methoxylated derivatives of indigotin and thioindigo. V. M. RODIONOV and B. M. BOGOSLOVSKI (J. Gen. Chem. Russ., 1937, 7, 2685—2692).—6-Amino-2:3-dimethoxybenzoic acid (I) and CH₂Cl·CO₂H in aq. Na₂CO₃ (4.5 hr. at 100°) yield 2-carboxy-3:4-dimethoxyphenylglycine (II), m.p. 160—161°; under similar conditions 2-amino-3:4-dimethoxybenzoic acid (III) does not react. When heated with KOH at 200° for 10 min. (II) affords probably 4:4'-dihydroxy-5:5'-dimethoxyindigotin, which with Me₂SO₄ gives 4:5:4':5'-tetramethoxyindigotin (IV). Diazotised (III) in dil. HCl and Na₂S₂ at 0° yield 6:6'-dicarboxy-2:3:2':3'-tetramethoxydiphenyl disulphide (V), m.p. 184—185°, reduced by Zn in aq. NaOH to 3:4-dimethoxythiosalicic acid, m.p. 201—202°, which does not condense with CH₂Cl·CO₂H. 2:2'-Dicarboxy-3:4:3':4'-tetramethoxydiphenyl disulphide, m.p. 127—129°, prepared similarly to (V), is reduced to 5:6-dimethoxythiosalicic acid, m.p. 153—154°, a solution of which in aq. NaOH condensed with CH₂Cl·CO₂H (90 min. at 100°) to S-2-carboxy-3:4-dimethoxyphenylthioglycolic acid, m.p. 141—142°. A solution of this in PhNO₂ boiled for 5 hr. gives 4:5:4':5'-tetramethoxythioindigo; this and (IV) are brown vat dyes. R. T.

Indole-indigo dyes.—See B., 1938, 356.

Heavy-metal derivatives of the metallic carbonyl hydrides.—See A., 1938, 1, 266.

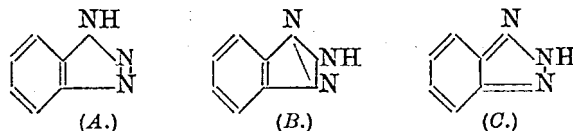
Diazapyrenes and diazaperylene.—See B., 1938, 354.

Stereochemistry of metallic derivatives of pyrromethenes. C. R. PORTER (J.C.S., 1938,

368—372).—The stereochemistry of the 4-covalent metallic derivatives is discussed, and it is shown on theoretical grounds that a planar configuration is impossible for simple salts of the type R₂M, where RH is the pyrromethene. Et 3:3':5:5'-tetramethylpyrromethene-4:4'-dicarboxylate (I) and excess of K₂PdCl₄ with NaOAc give a mixture from which can be isolated *bis*-(4:4'-dicarbethoxy-3:3':5:5'-tetramethylpyrromethene)dipalladous dichloride, R₂Pd₂Cl₂, decomp. 235°, and the monopalladous chloride, R₂HPdCl, decomp. 170—200°, which with EtOH affords *bis*-(4:4'-dicarbethoxy-3:3':5:5'-tetramethylpyrromethene)palladium, R₂Pd, decomp. 322°. Excess of HgCl₂, NaOAc, and (I) give a product, RHgCl, m.p. 214—216°, excess of Hg(NO₃)₂ or HgSO₄ in AcOH yields a substance, RHg·OAc, m.p. 217—220° (decomp.), and equiv. amounts of (I) and Hg(NO₃)₂ afford a compound, R₂Hg, m.p. 227—230° (decomp.). The Cd derivative of (I) decomposes at 235—245°. Et 3:3'-dimethylpyrromethene-4:4'-dicarboxylate gives the following salts: Co, m.p. 340° (decomp.), Ni, m.p. 315° (decomp.), Cu, m.p. 305° (decomp.), Zn, m.p. 302° (decomp.), and Cd, m.p. 316° (decomp.).

F. R. S.

Spectrochemistry and structure of benzotriazoles. K. VON AUWERS (Ber., 1938, 71, [B], 604—610).—The spectrochemical data of many benzotriazoles in substance and in quinoline are recorded.



To 1-derivatives, obtained by known methods, only (A) is applicable. For 2-derivatives it is impossible to choose between (B) and (C) but in favour of (C) it is noted that 2-alkylbenzotriazoles have exaltations similar to those of the 2-alkylindazoles of established quinonoid structure. Further, as with the indazoles the mol. refraction and mol. dispersion of 2-derivatives exceeds that of the 1-isomerides. Compounds of structure (C) are less saturated than the benzenoid compounds of structure (A) and therefore tend more to exaltations. Between (A) and (B) there is no marked difference in the degree of saturation. Finally examination of the model shows that dicyclic structures (C) are formed without strain and represent closed systems; this is not true in the same degree of the tricyclic structure (B). Spectroscopically benzotriazole itself resembles its 1-derivatives. Contrary to the literature, *o*-C₆H₄(NMe₂)₂, from *o*-C₆H₄(NH₂)₂, MeI, and MeOH at 180°, is a stable, colourless liquid, b.p. 101.5—102.5°/15 mm., whereas tetramethyl-*m*-phenylenediamine, b.p. 144—145°/18 mm., darkens very rapidly when kept. H. W.

N-Alkylbenzotriazoles and the constitution of benzotriazoles. F. KROLLPFEIFFER, H. PÖTZ, and A. ROSENBERG (Ber., 1938, 71, [B], 596—603).—Benzotriazole (I), like its 1-alkyl derivatives, is sol. in dil. HCl and is immediately and quantitatively pptd. as hydrochloride by HCl from Et₂O. 2-Alkylbenzotriazoles are insol. in dil. HCl and are not pptd. by HCl from Et₂O. The ultra-violet absorption spectra

of (I) and of its 1-Me-derivative are very similar and hence (I) is $C_6H_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} N$. It is not possible to decide between the formulæ (B) and (C) (preceding abstract) for 2-substituted benzotriazoles, which probably represent different "electronic conditions" of these compounds. The following compounds are obtained by methods described previously: 1-, b.p. 160—162°/15 mm., m.p. 32—33°, and 2-, b.p. 124—126°/16 mm., *n*-propylbenzotriazole; 1-, b.p. 170—172°/17 mm., and 2-, 137—139°/16 mm., *n*-butylbenzotriazole; 1-, m.p. 115—116°, and 2-, b.p. 168—169°/1 mm., m.p. 36.5—37.5°, *benzylbenzotriazole*; 1-, m.p. 90—91° (*benzoate*, m.p. 104—105°), and 2-, m.p. 70—71° (*benzoate*, m.p. 74—75° after softening), β -hydroxyethylbenzotriazole, whence (by HBr) 1-, m.p. 119—120°, and 2-, m.p. 59—60°, β -bromoethylbenzotriazole; 1-, b.p. 117—118°/3 mm., m.p. 29—30°, and 2-, b.p. 84—84.5°/3 mm., *vinylbenzotriazole*, from the requisite Br-compounds and 2*N*-NaOH. With the necessary bromoethyl derivative and NaOMe in MeOH (I) gives $\alpha\beta$ -di-1:2-benzotriazylethane, m.p. 136—137°, $\alpha\beta$ -di-2:2-, m.p. 152—153°, and $\alpha\beta$ -di-1:1-benzotriazylethane, m.p. 161—162°, also obtained from (I) and $C_6H_4Br_2$. Addition of $ClCO_2Et$ to 2*N*-NaOH and (I) affords Et 1-benzotriazylformate, m.p. 71—72° (corresponding *Me* ester, m.p. 80—81°); the 2-derivative does not appear to be formed. Thermal decomp. of the esters gives mixtures of the corresponding 1- and 2-alkylbenzthiazoles. 2-Benzylbenzthiazole and Me_2SO_4 give 2-benzyl-1-methyl-1:2:3-benzotriazolium methosulphate, m.p. 143—144°, converted by boiling $Na_2S_2O_4$ and conc. NH_3 into 1-methylbenzotriazole and transformed by 2*N*-NaOH into a substance, $C_{14}H_{13}N_3$, m.p. 78—79°, which passes when distilled in a high vac. into a compound, $C_{14}H_{13}N_3$, m.p. 132—133°.

H. W.

Toxoflavin; an isomeride of 1-methylxanthine. A. G. VAN VEEN and J. K. BAARS (Rec. trav. chim., 1938, 57, 248—264; cf. A., 1934, 537).—Toxoflavine (I), $NMe \cdot CO \cdot C \cdot N \begin{smallmatrix} \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} NH \cdot C \cdot N > CH_2$, is stated to be a cyclic diimine of alloxan. With $KClO_3$ -HCl at 50° it yields methylalloxan; with alkaline $KMnO_4$ at 0° it gives a substance, $C_6H_7ON_5$, m.p. 220°, and with $o\text{-}C_6H_4(NH_2)_2$ -HCl at room temp. it gives *N*-methylalloxazine, m.p. 330° with sublimation. When (I) is reduced (H_2 -Pt) in AcOH and the product treated with HCl *N*-methyluramil is obtained; with aq. HCl (I) yields toxoflavine hydrate, m.p. 250° (partly sublimed at 200°), oxidised by $KClO_3$ -HCl to 5:5'-dichloro-*N*-methylbarbituric acid. The unusual properties of (I) are due to the position of the double linkings.

A. T. P.

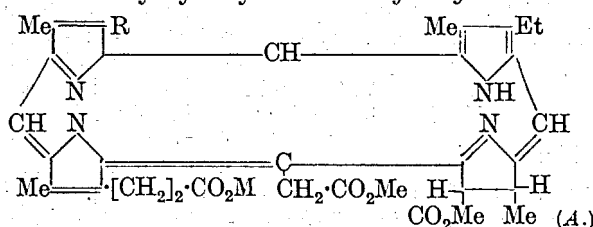
Spontaneous polymerisation of cyanoacetyl chloride. III. G. SCHROETER and E. FINCK (Ber., 1938, 71, [B], 671—684; cf. A., 1932, 526).— $CN \cdot CH_2 \cdot COCl$ is obtained economically by passing Cl_2 into a solution of $CN \cdot CH_2 \cdot CO_2H$ and PCl_3 in Et_2O ; it is largely unchanged by distillation in a high vac. (b.p. 59°/0.05 mm., 61°/0.1 mm., 68°/0.2 mm.) and the P-free material thus obtained polymerises in the same manner as the crude product to 6-chloronorcinine (I) [6-chloro-2:4-dihydroxynicotinonitrile].

The corresponding amide is converted by $NaNO_2$ in conc. H_2SO_4 into 6-chloro-2:4-dihydroxynicotinic acid, m.p. 226° (decomp.) [NH_4 , *Ca*, *Ba*, and *Pb* salts; the *Me* ester, m.p. 154°, is converted by $NHET_2$ into 6-chloro-2:4-dihydroxypyridine, m.p. 234° (decomp.), also derived from the acid and boiling, fuming HCl]. With a deficiency of PCl_5 at 150° (I) gives 4:6-dichloro-2-hydroxynicotinonitrile (II) (*Na*, *K*, NH_4 , *Ba*, *Cu*, *Ag*, *Pb*, and *Ca* salts) and 2:4:6-trichloronicotinonitrile (III), converted into (II) by warm 2*N*-NaOH. With Zn dust and 2*N*- H_2SO_4 (II) gives 2-hydroxynicotinonitrile, m.p. 224° (*Na*, NH_4 , *Ca*, and *Ag* salts). Na_2S and (III) yield 4:6-dichloronicotinonitrile-2-thiol (*Na*, *Ag*, *Cu*, and *Pb* salts). $N_2H_4 \cdot H_2O$ and (III) yield 6-chloro-4-hydrazino-2-hydroxynicotinonitrile, which darkens at 150° and becomes decomposed without melting; it does not give a tetrazole derivative. Boiling 34% CH_2O converts (I) into 6-chloro-2:4-dihydroxy-5-hydroxymethylnicotinonitrile [Na_2 (+2*H*₂*O*) (IV), *Cu*₂ (+2*H*₂*O*), *Cu* (+4*H*₂*O*), *Na* (+2*H*₂*O*), and *Ag* salts], transformed by Ac_2O and conc. H_2SO_4 into 6-chloro-2:4-dihydroxy-5-acetoxymethylnicotinonitrile, m.p. >300° after softening at 130° (*Pb*, *Cu*, and *Ag* salts). When heated at 135° (IV) gives the cyclic anhydride of methylenedichloronor-cicimine, $OH \cdot C \cdot C(CN) : C \cdot O - C \cdot C(CN) \cdot C \cdot OH$
 $\quad \quad \quad N - CCl_2 \cdot CH_2 \cdot CCl_2 \cdot N$

[Na_2 (+3*H*₂*O*) and *Cu* (+4*H*₂*O*) salts]. Me_2SO_4 transforms (IV) into 6-chloro-5-hydroxymethylricininic acid, m.p. 135° (*Ac* derivative, m.p. 120—121°). $NHET_2$ and $NHPh \cdot NH_2$ do not remove Cl from (I) at 170°. $N_2H_4 \cdot H_2O$ and (I) at 100° yield 6-hydrazino-2:4-dihydroxynicotinonitrile (V). (+*H*₂*O*), decomp. 260° (*Na*, and Na_2 salts; benzylidene and piperonylidene derivatives). It is converted by conc. H_2SO_4 at 100° into 6-hydrazino-2:4-dihydroxynicotinamide (NH_4 , *Ba*, and *Pb* salts; benzylidene and piperonylidene derivatives), whereas 6-hydrazino-2:4-dihydroxynicotinohydrazide (dihydrochloride) is obtained from $N_2H_4 \cdot H_2O$ and 6-chloro-2:4-dihydroxynicotinamide. 6-Chlororicininic acid and $N_2H_4 \cdot H_2O$ at 100° yield 6-hydrazinoricininic acid (*Na* salt; benzylidene compound). 6-Chlororicinine affords 6-hydrazinoricinine (hydrochloride; nitrate; benzylidene compound), which with $CH_3Ac \cdot CO_2Et$ yields 5-ricinylmethylpyrazolone, m.p. 206° (decomp.). $NaNO_2$ and conc. H_2SO_4 convert (V) into 1:3-diketotetramethylenetetrazole-2-nitrile, $N \begin{smallmatrix} \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C \cdot CH_2 \cdot CO$
 $\quad \quad \quad N - N - CO - CH_2 \cdot CN$ [Na_1 (+2*H*₂*O*) and *Na* (+5*H*₂*O*) salts], oxidised by $KMnO_4$ to tetrazole-5-carboxylic acid (*Ag* salt), which in boiling H_2O passes into tetrazole. 1:3-Diketotetramethylenetetrazole-2-carboxylamide (VI) [NH_4 , *Na*, *Ca*, *Ba*, *Pb*, NH_4 , *Ba* (+3*H*₂*O*), and Na_2 (VII) (+3*H*₂*O*) salts] is converted by boiling 2*N*-HCl or EtOH into the ether, $(C_6H_4O_2N_5)_2O$, which yields salts sparingly sol. in H_2O . Me_2SO_4 and (VII) give the ether, $C_6H_4O_2N_5 \cdot OMe$; CH_2O and (VI) readily give a $OH \cdot CH_2$ compound [Na_2 (+3*H*₂*O*) salt]. 1:3-Diketotetramethylenetetrazole-2-carboxylic acid (VIII), m.p. 195° (decomp.), gives NH_4 , Na_1 (+2*H*₂*O*), *Ba*, *Ca*, *Pb*, *Cu*, and *Ag* salts; the *Me* ester has m.p. 198° (decomp.). Boiling H_2O transforms (VIII) into 5-acetonyltetrazole, m.p. 114° [sparingly sol. *Ag* and *Cu* salts; semicarbazone, m.p. 201° (decomp.); oxime,

m.p. 155—156°], transformed by Me_2SO_4 in alkaline solution into 5-acetonyl-1-methyltetrazole, m.p. 73—74° (semicarbazone, m.p. 152—153°). H. W.

Chlorophyll. LXXXII. Partial syntheses of dehydrobacteriophorbide and dehydrobacteriochlorin. H. FISCHER, W. LAUTSCH, and K. H. LIN (Annalen, 1938, 534, 1—22; cf. A., 1937, III, 486).—Further evidence is adduced in favour of the constitution assigned previously to dehydrobacteriophorbide. The occurrence of a *b*-component during the growth of the purple bacteria is disproved. Bacteriochlorophyll (I) is homogeneous and the proof is important since it strengthens the view that chlorophyll *b* (II) is a secondary oxidation product of chlorophyll *a*. (I) is regarded as a precursor of chlorophyll, merely requiring transformation of Ac into $\cdot\text{CH}\cdot\text{CH}_2$. (II) results by secondary oxidation of Mo at $\text{C}_{(3)}$. Chlorin e_6 Me_3 ester is shaken with $\text{HBr}\cdot\text{AcOH}$ and the unstable additive product (III) is immediately hydrolysed to 2- α -hydroxymesochlorin



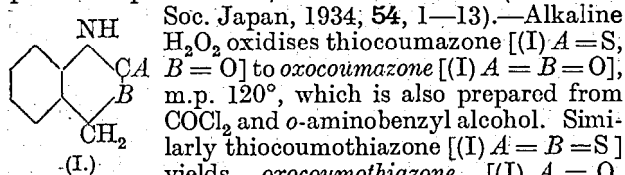
e_6 Me_3 ester [(A) R = $\text{CHMe}\cdot\text{OH}$], m.p. 215°, oxidised by KMnO_4 in $\text{C}_5\text{H}_5\text{N}$ to acetylchlorin e_6 Me_3 ester (IV) [(A) R = Ac], identical in m.p. and crystal form with the natural material but having $[\alpha]_D -423^\circ$ in place of -86° [oxime, m.p. 132—135°; salt (V), $\text{C}_{37}\text{H}_{40}\text{O}_7\text{N}_4\text{Zn}$, m.p. 214—216°]. This is converted by $\text{KOH}\cdot\text{MeOH}\cdot\text{C}_5\text{H}_5\text{N}$ into 2-acetylmethylphæophorbide-*a* identical with the material derived from (I). NaOAc and (III) readily afford 2- α -acetoxymesochlorin e_6 Me_3 ester, m.p. 117—118°, whilst 2- α -methoxymesochlorin e_6 Me_3 ester, m.p. 170°, is smoothly obtained with boiling MeOH . $\text{KOH}\cdot\text{PrOH}$ converts (IV) in $\text{C}_5\text{H}_5\text{N}\cdot\text{Et}_2\text{O}$ into acetylpuropurin 7 Me_3 ester, m.p. 258—260°, and 2-devinylacetylpuropurin 18 Me ester, m.p. 304—305°, the former of which passes in boiling $\text{C}_5\text{H}_5\text{N}$ into ketorhodoporphyrin Me_2 ester. Hydrogenation (Raney Ni) of (V) in dioxan and treatment of the solution with air regenerates (V), but if reaction is effected at 85° and the resulting solution is treated with FeCl_3 chloroketoporphyrin e_6 results. Hydrogenation (PtO_2 in MeOH) of (V) causes partial conversion of CO into $\text{CH}\cdot\text{OH}$ whereas in dioxan at 85—90° reduction does not occur. H. W.

Chloro- and bromo-phthalocyanines.—See B., 1938, 356.

New synthetic method in the pyrazole group. III. Pyrazolo-triazines and -pyrimidines. R. JUSTONI and R. FUSCO (Gazzetta, 1938, 68, 59—76; cf. A., 1937, II, 261; 1938, II, 190).—The Na derivatives of $\text{CN}\cdot\text{CH}_2\text{R}$, where R = CN, $\text{CO}\cdot\text{NH}_2$, and $\text{CO}\cdot\text{NHMe}$, with $\text{CPhCl}\cdot\text{N}\cdot\text{NHPh}$ yield respectively 5-amino-4-cyano-1:3-diphenylpyrazole (I), m.p. 168° (Ac derivative, m.p. 203°), and 5-amino-1:3-diphenylpyrazole-4-carboxylamide (II), m.p. 186—

187°, and -carboxylmethylamide (III), m.p. 153°. Mild treatment of (I) with alkali has no action, and vigorous treatment causes complete breakdown. Conc. HCl has no action at the b.p., but at 160° converts (I) and (II) into 5-amino-1:3-diphenylpyrazole (Ac derivative, new m.p. 152.5°). With HNO_2 , (II) gives 6-hydroxy-1':3'-diphenylpyrazolo-5':4'-4:5-1:2:3-triazine, m.p. 160° (decomp.) (Na salt, m.p. 230—240°). The Ac derivative, m.p. 242.5°, of (II) is converted by heating into 6-keto-1':3'-diphenyl-2-methyl-1:6-dihydropyrazolo-5':4'-4:5-pyrimidine, m.p. 296°. With HNO_2 , (III) gives 6-keto-1':3'-diphenyl-1-methyl-1:6-dihydropyrazolo-5':4'-4:5-1:2:3-triazine, m.p. 155.5°. Cyanoacetmethylamide, m.p. 98°, is prepared from $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and NH_2Me . The Na derivative of $\text{CH}_2(\text{CN})_2$ and BzCl give, not the (unknown) $\text{COPh}\cdot\text{CH}(\text{CN})_2$, but a substance, m.p. 126—127° (decomp.), which with $\text{NHPh}\cdot\text{NH}_2$ yields a substance, m.p. 134—135° (decomp.). E. W. W.

Action of hydrogen peroxide on organic sulphur compounds. I, II. R. KITAMURA (J. Pharm. Soc. Japan, 1934, 54, 1—13).—Alkaline H_2O_2 oxidises thiocoumazon [(I) A = S, B = O] to oxocoumazon [(I) A = B = O], m.p. 120°, which is also prepared from COCl_2 and *o*-aminobenzyl alcohol. Similarly thiocoumothiazone [(I) A = B = S] yields oxocoumothiazone [(I) A = O, B = S], m.p. 153.5—154.5°. The method is applicable to a wide range of S compounds; its application on a quant. basis is described. CH. ABS. (r)



Unsaturation and tautomeric mobility of heterocyclic compounds. XI. α - and β -Naphthoxazole and 5-bromobenzoxazole derivatives. Ultra-violet absorption spectra of some tautomeric selenazoles. R. D. DESAI, R. F. HUNTER, and A. R. K. KHALIDI (J.C.S., 1938, 321—329).—The ultra-violet absorption spectrum of 1-hydroxybenz-selenazole in MeOH is almost identical with that of the *N*-Me ether, showing that the covalent form of the mol. has the ketodihydro-structure. In aq. NaOH , there is a drop in the first max. between 2800 and 2900 Å., and a shift of the curve towards the region of longer λ . The curve of 1-thiobenz-selenazole in MeOH also indicates that this mol. has the thiodihydro-structure. In aq. NaOH , there is a slight shift towards the region of shorter λ , and an appreciable drop in the first max. connected with the ionisation of the H of the triad system.

The α - and β -naphthoxazoles containing prototropic triad systems exhibit a close analogy with their thiazole analogues in their behaviour toward methylating agents. 1-Amino- α -naphthoxazole and its β -analogue react exclusively in the amino-aromatic form with MeI , yielding iminomethyldihydro-derivatives. The Ph in anilinonaphthoxazoles enables the N to which it is attached to compete with the ring N during methylation. The hydroxy- and thiol-naphthoxazoles also resemble their benzoxazole analogues on methylation.

2-Amino- α -naphthol hydrochloride and KCNS give 1-hydroxy-2-naphthylthiourea, m.p. 252°, which with HgO followed by NaOH forms 1-amino-

α -naphthoxazole, m.p. 195° (Ac derivative, m.p. 210°), methylated (MeI) to 1-imino-2-methyl-1:2-dihydro- α -naphthoxazole, m.p. 154° (Ac derivative, m.p. 133°). 1-Thiol- α -naphthoxazole with NH_2Me gives 1-methylamino-, m.p. 160° (Ac derivative, m.p. 136°), and with NH_2Ph yields 1-anilino- α -naphthoxazole, m.p. 236°, methylated to 1-phenylimino-2-methyl-1:2-dihydro- (picrate, m.p. 188°; 75%) and 1-phenylmethylamino- α -naphthoxazole (picrate, m.p. 208°). 1-Hydroxy- α -naphthoxazole, m.p. 218—220°, obtained from 2:1- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ and ClCO_2Et or COCl_2 , is methylated to 1-keto-2-methyl-1:2-dihydro- α -naphthoxazole, m.p. 198°. 2-Hydroxy-1-naphthylthiocarbamide, decomp. about 300°, with $\text{HgO}\cdot\text{NaOH}$, affords 2-amino- β -naphthoxazole, m.p. 176° (Ac derivative, m.p. 112°), methylated to 2-imino-1-methyl-1:2-dihydro- β -naphthoxazole, m.p. 148—150° (Ac derivative, m.p. 132°). 2-Thiol- β -naphthoxazole with NH_2Me yields 2-methylamino-, m.p. 158° (Ac derivative, m.p. 140°), and with NH_2Ph forms 2-anilino- β -naphthoxazole, m.p. 172°, methylated to 2-phenylimino-1-methyl-1:2-dihydro- (picrate, m.p. 174—176°; 75%) and 2-phenylmethylamino- β -naphthoxazole (picrate, m.p. 194—196°). 2-Hydroxy- β -naphthoxazole, m.p. 208°, prepared from 1:2- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ and ClCO_2Et or COCl_2 , is methylated to 2-keto-1-methyl-1:2-dihydro- β -naphthoxazole, m.p. 188°, which with P_2S_5 gives 2-thio-1-methyl-1:2-dihydro- β -naphthoxazole, m.p. 180°. 2-Thiol- β -naphthoxazole and MeI afford the S-Me ether, m.p. 66—68°.

5-Nitro-2-aminophenol and ClCO_2Et yield 4-nitro-2-hydroxyphenylurethane, m.p. 174°, which when heated forms 5-nitro-1-hydroxybenzoxazole, m.p. 244—246°, reduced to the 5- NH_2 -derivative, m.p. 204° (Ac derivative, m.p. 234°). The NH_2 -compound is converted into 5-bromo-1-hydroxybenzoxazole, m.p. 188—190°, methylated to 5-bromo-1-keto-2-methyl-1:2-dihydrobenzoxazole, m.p. 150°, also obtained by bromination of 1-keto-2-methyl-1:2-dihydrobenzoxazole. 5-Nitro-1-thiolbenzoxazole, m.p. 216—218°, obtained from 5-nitro-*o*-aminophenol and $\text{CS}_2\cdot\text{KOH}$, is reduced to the 5- NH_2 -compound, m.p. 228°, converted into the 5-Br-compound, m.p. 198—200°. This is methylated to 5-bromo-1-methylthiolbenzoxazole, m.p. 148°. F. R. S.

Thiazole derivatives of alanine. B. HOLMBERG (Compt. rend. Trav. Lab. Carlsberg, 1938, 22, 211—218).—*dl*-Alanine (I), NaOH , and CS_2 followed by $\text{CH}_2\text{Cl}\cdot\text{COMe}$ give acetonil trithiocarbonate, m.p. 58—59° and 73—74°, and 4-methyl-2-thionthiazoline-3- α -propionic acid, m.p. 172—173°, which with (—)- α -CHPhMe $\cdot\text{NH}_2$ forms a salt, m.p. 178—179°, yielding the inactive form of the acid. The active form of the acid, m.p. 153—154°, $[\alpha]_D +16.4^\circ$ in COMe_2 , is obtained from *d*-alanine. Similarly, (I) and $\text{COPh}\cdot\text{CH}_2\text{Br}$ yield *dl*-phenacyldithiocarbaminy- α -propionic acid, m.p. 154—155°, which with AcOH affords 4-phenyl-2-thionthiazoline-3- α -propionic acid, m.p. 189—190° (active acid, m.p. 188—189°, $[\alpha]_D -34.1^\circ$ in COMe_2). $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ and (I) similarly give thiocarbonylalaninethioglycolic acid (+ H_2O), m.p. 90—92°, converted (HCl) into 4-keto-2-thionthiazolidine-3- α -propionic acid [rhodanine- α -propionic

acid], m.p. 121—123° and 143—144°, obtained in active form from *l*(+)-alanine, m.p. 152—153°, $[\alpha]_D -47.2^\circ$ in COMe_2 . F. R. S.

Benzthiazole derivatives. II. Preparation of 1-chlorobenzthiazole and certain of its derivatives. N. S. DROZDOV and V. I. STAVROVSKAJA (J. Gen. Chem. Russ., 1937, 7, 2813—2818).—1-Thiolbenzthiazole (I), nitrated at 0°, yields 6-nitro-1-thiolbenzthiazole (II), m.p. 255°, reduced by H_2S to 6-amino-1-thiolbenzthiazole, m.p. 260—261°, converted by the Sandmeyer reaction into 6-chloro-, m.p. 244—245°, and 6-iodo-1-thiolbenzthiazole, m.p. 233—234°. (I) in POCl_3 and PCl_5 (3 hr. at 95—130°) yield chiefly 1-chlorobenzthiazole (III), together with di-2-benzthiazolyl sulphide, the yield of which is greater at higher than at lower temp. 1-Chloro-6-nitrobenzthiazole is prepared by nitration of (III), or from (II) and PCl_5 . R. T.

Benzthiazoles.—See B., 1938, 354.

Thiazoles and benzthiazoles.—See B., 1938, 413.

Quinoline derivatives. III. T. N. GHOSH (J. Indian Chem. Soc., 1937, 14, 713—716).—Et 3:4-dihydroxythiophen-2:5-dicarboxylate and NH_2Ph give 2:5-diphenylcarbamy-3:4-dihydroxythiophen, m.p. 292—293° (decomp.) which with H_2SO_4 yields 4-hydroxythiopheno-2:3(3':4')-2'-hydroxyquinoline-7'(?)-sulphonic acid, m.p. >310°, the SO_3H being stable to HBr . Et 3:4-dihydroxy-1-phenylpyrrolidine-2:5-dicarboxylate does not condense with NH_2Ph . 2-Methylbenziminazole and $\text{Et}_2\text{C}_2\text{O}_4$ afford $\alpha\delta$ -dibenziminazolyl- $\beta\gamma$ -diketobutane, m.p. >300°, which does not react with *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$. F. R. S.

Preparation of amorphous quinine iodobismuthate. A. M. DE CASTILHO (Boll. Chim. farm., 1938, 77, 149—152).—A modification of the method of François and Seguin (A., 1925, i, 1084) yields a product of uniform colour and composition [corresponding with Bi: quinine (B) = 1:28; $\text{B}_2\text{HI}_2\text{BiI}_3$]. F. O. H.

Constitution of some alkaloidal derivatives of Cinchona alkaloids. E. LÉGER (Bull. Soc. chim., 1938, [v], 5, 183—186; cf. A., 1888, 380; 1919, i, 170, 451).— α - and β -Hydroxydihydrocinchonines [from cinchonine (I) and H_2SO_4] contain *cis*- and *trans*-forms of $-\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{OH}$. With H_2SO_4 the α -compound gives a *cis*-form corresponding with hydroxydihydroepicinchonine, dehydrated to cinchonine, in agreement with the formation of *epi*hydrocinchonine from hydrocinchonine and H_2SO_4 (cf. Fiedzinsko and Suszko, A., 1935, 765). With KOH or AgOH hydrohalides of (I) give products identical with those from (I) and H_2SO_4 , viz., *apocinchonine* (II), cinchoniline (III), and cinchonine (IV). The formation of (III) and (IV) from (I) is analogous to that of γ - and α -isoquinidines from quinidine (cf. Domanski and Suszko, A., 1935, 874, 1137), indicating that these isoquinidines are derived from hydroxydihydroquinidines and thus correspond structurally with (III) and (IV) respectively. Cinchonidine with H_2SO_4 gives a hydroxydihydrocinchonidine, dehydrated to two bases corresponding with (II). E. G. B.

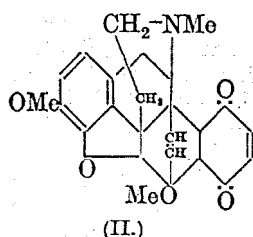
Hydrogenation of yohimbine. R. MAJIMA and S. MURAHASHI (Coll. Papers Fac. Sci. Osaka, 1935, 2, 341—344).—Treatment of yohimbic acid successively with maleic acid and Pt yields *tetrahydro-yohimbic acid*, m.p. 335° (decomp.), methylated to *tetrahydroyohimbine*, m.p. 256—256.5°, $[\alpha]_D^{25} + 289.9^\circ$. Deoxy-yohimbic acid similarly gives *tetrahydrodeoxy-yohimbic acid* and *tetrahydrodeoxy-yohimbine*, decomp. 251°.

CH. ABS. (r)

Strychnos alkaloids. XCVIII. Reactions of the bases obtained from *N*-methyl-*sec*- ψ -strychnine methiodide with sodium amalgam and sodium methoxide. H. LEUCHS (Ber., 1938, 71, [B], 660—667; cf. A., 1938, II, 73).—Reduction of *N*-methyl-*sec*- ψ -strychnine methiodide (I) by Na-Hg gives the *methoxy-base* (II), $C_{23}H_{28}O_3N_2$, m.p. 170—172° (vac.) [*perchlorate*, m.p. 239—243° (decomp.); *hydrobromide*, m.p. 215° (decomp.)], with unchanged material isolated as the *hydrobromide*, m.p. 235—240° (decomp.). Hydrogenation of (II) gives the *base*, $C_{23}H_{30}O_3N_2$, m.p. 214° (vac.) [*perchlorate*]. The successive action of Me_2SO_4 and $HClO_4$ on (I) leads to the *methoperchlorate*, $C_{23}H_{28}O_3N_2 \cdot MeClO_4$, m.p. 275° (decomp.) after softening and darkening; the corresponding base is hydrogenated (PtO₂) to the *tert. base*, $C_{24}H_{34}O_3N_2$, m.p. 128° (vac.) [*perchlorate*, m.p. 245—248° (slight decomp.); *methiodide*, m.p. 270—273°]. The ether (III), $C_{23}H_{26}O_3N_2$ (A., 1937, II, 435) is oxidised by $AgOAc$ in $2N$ - $AcOH$ and the product when treated with N - $HClO_4$ gives the *salt*, $C_{22}H_{25}O_4N_2 \cdot ClO_4$, m.p. 305° (decomp.), hydrogenated to the *compounds*, $C_{22}H_{27}O_3N_2 \cdot ClO_4$, m.p. 275° (decomp.), and $C_{22}H_{29}O_3N_2 \cdot ClO_4$, m.p. 205°. Hydrogenation of (III) followed by treatment with MeI yields the *methiodide*, $C_{24}H_{32}O_3N_2 \cdot MeI$, m.p. 293—295° (vac.; decomp.), and the *base*, $C_{22}H_{26}O_3N_2$, m.p. 132° [*perchlorate*, m.p. 250—255° (decomp.)]. Hydrogenation of (I) gives the *base*, $C_{22}H_{28}O_3N_2$, m.p. 197° (vac.). The *methiodide*, $C_{23}H_{26}O_3N_2 \cdot MeI$ (A., 1938, II, 73), is hydrogenated to the *salt*, $C_{24}H_{30}O_3N_2 \cdot HI$, and a *base*, $C_{23}H_{30}O_3N_2$, m.p. about 73° after softening at 65° [*perchlorate*, m.p. about 260° (decomp.) after softening at 220°]. The isomeric *methiodide*, $C_{23}H_{26}O_3N_2 \cdot MeI$ (*loc. cit.*), absorbs 6 H when hydrogenated (PtO₂).

H. W.

Additive compounds of thebaine with dienes. W. SANDERMANN (Ber., 1938, 71, [B], 648—650).—



(II.)

Thebaine (I) and *p*-benzoquinone in boiling $EtOH$ readily give the sulphur-yellow *adduct* (II), m.p. 247—249° with darkening after becoming colourless (*hydrobromide*), which is isomerised in boiling $EtOH$ to a colourless *compound*, $C_{25}H_{25}O_5N$, m.p. 247—249° after darkening at 220°.

With

1:4-naphthaquinone and maleic anhydride (I) gives *adducts*, m.p. 239—240°, and 263—264° after darkening at 260°, respectively.

H. W.

Alkaloids of *Veratrum album*. III. Jervine, ψ -jervine, and rubijervine. W. POETHKE (Arch. Pharm., 1938, 276, 170—181; cf. A., 1938, II, 35).—

Jervine [*sulphate*, m.p. 297—298° (corr.) (also *di-hydrate*); *trichloroacetate* (loses $CCl_3 \cdot CO_2H$ at 100°), Ac_2 derivative; *di-p*-bromobenzoyl derivative, m.p. 280—282° (corr.)] contains 2 OH (Zerevitinov) but no CH_2O_2 : ψ -jervine, m.p. 304—305.5° (corr.; decomp.); $C_{35}H_{49}O_8N$, contains 4 OH and NH , but neither OMe nor CH_2O_2 . It yields a *hydrochloride*, m.p. 254—256° (corr.; decomp.), a *hydrothiocyanate*, m.p. 245.5—246° (corr.; decomp.), a *picrate*, and a *NO*-compound, m.p. 261° (corr.; decomp.). Rubijervine, m.p. 239—240° (corr.; decomp.) (*mono-hydrate*), contains 2 OH (Zerevitinov) and yields a *hydriodide*, m.p. 261—262° (corr.; decomp.), and a *p*-bromobenzoate, m.p. 254—256° (corr.; decomp.).

J. D. R.

Azo dyes and immunobiology. "Diazotisation" of salvarsan. H. E. FIERZ, W. JADASSOHN, and A. MARGOT (Helv. Chim. Acta, 1938, 21, 280—293).—Addition of $NaNO_2$ to a solution of salvarsan (I) in HCl at 0° gives immediately an intensely yellow solution which remains clear until 1.5 mols. of $NaNO_2$ have been added. Reaction with KI-starch paper is not observed until after the addition of 3.6—3.8 mols. of $NaNO_2$. The change cannot be quantitatively followed by coupling with components. "Diazotisation" of (I) in neutral solution in presence of Cu or of a Zn salt does not give a product capable of coupling. Examination of the oxidation of the arseno-group of (I) during diazotisation by titration with I shows that this occurs immediately in acid solution, being thus in contrast with atm. oxidation. After complete "diazotisation" (until the solution reacts with KI-starch paper) (I) is not completely oxidised to the arsenic acid, which does not react with I; actually the consumption of I is about 40% of that of the non-diazotised solution. "Completely diazotised" solutions of (I) do not contain unchanged (I), non-diazotised As aminohydroxyphenyl oxide (II), or non-diazotised aminohydroxyphenylarsinic acid (III). Diazotisation of (III) occurs normally in acid solution whereas (II) suffers oxidation although after "complete diazotisation" it is not wholly oxidised to the phenylarsinic acid, an equilibrium being set up. The ppt. obtained by diazotisation of (I) contains compounds of As^{III} and As^V which do not couple. Derivatives changed at the NH_2 -OH grouping and their degradation products are mainly present. The solution contains a mixture of compounds including coupling derivatives of As^{III} . Diazotisation of (I) in HCl involves immediate oxidation of the As_2 group. Attempts to couple diazotised (I) or (III) with horse serum and tyrosine in presence of Na_2CO_3 , $AcOH$, MgO , $Ca(OH)_2$, or $Na(OH)_2$ were unsuccessful.

H. W.

Mercuri-organic compounds. XV. Structure of products of addition of mercury salts to styrene and α -methylstyrene. A. N. NESMEJANOV and R. C. FREIDLIN (J. Gen. Chem. Russ., 1937, 7, 2748—2753).—Styrene and aq. $Hg(OAc)_2$ yield *phenylacetmercurimethylcarbinol*, m.p. 77—79° (decomp.), reduced by Na-Hg in H_2O to $CHPhMe \cdot OH$, and converted by aq. KCl or KBr into *phenylchloro*, m.p. 95—96°, or *phenylbromo-mercurimethylcarbinol*, m.p. 102—103°. $CPhMe \cdot CH_2$ and aq. $Hg(OAc)_2$ give β -*phenyl- α -acetmercuripropen- β -ol*, m.p. 101—102°, from

which the corresponding *Cl*-, an oil, and *Br*-derivative, m.p. 45–46°, are prepared as above. R. T.

Crystalline salts derived from *p*-aminophenylstibonic acid. W. H. GRAY and I. D. LAMB (J.C.S., 1938, 401).—“Stibacetin” crystallises from H_2O in needles, decomp. 300°, containing 2–3 acetamidophenylstibonic acid residues to 1 Na. Hydrolysis of this with 7% NaOH at 90° for 7 hr. gives cryst. Na *p*-aminophenylstibonate (+2 H_2O). F. R. S.

Organometallic compounds of indium. W. C. SCHUMB and H. I. CRANE (J. Amer. Chem. Soc., 1938, 60, 306–308).—*InPh*₃, m.p. 291° (decomp.), from $HgPh_2$ and In (sealed tube) at 130°, reacts with the requisite halogen in C_6H_6 , to give compounds, *InPh*₂Br, m.p. <300°, *InPh*Br₂, m.p. <300°, *InPh*₂I, and *InPh*I₂. In reacts slowly with CH_2I_2 , probably forming *InI*₂· CH_2I . *InBr*₃ and dioxan in Et_2O give *InBr*₃·2 $C_4H_8O_2$, decomp. 140°. *InI*₃ and C_5H_5N give *InI*₃·3 C_5H_5N , m.p. 164°. The properties of the compounds are described. E. S. H.

Grignard compounds derived from pyridine. J. OVERHOFF and W. PROOST (Rec. trav. chim., 1938, 57, 179–184).—A Grignard compound (I), considered to be a complex C_5H_4NBr ·(C_5H_4NMgBr)_n, has been prepared from 2-bromopyridine (II) and Mg: (a) by the use of a catalyst prepared by boiling $C_2H_4Br_2$ containing Al, a few drops of this solution together with MeI added to an ethereal solution of (II) in contact with Mg giving a ppt. (I) which by treatment with PhCHO followed by NH_4Cl gives phenyl-2-pyridylmethanol (III) in 10–16% yield from the total reaction mixture; (b) by the interaction of (II) and Mg in the undiluted form, cooling in ice, and adding Et_2O as soon as a brown colour appears, the yield of (III) being 8–13%; (c) by using Grignard's “entrainment” method (A., 1934, 397), i.e., by simultaneous addition of org. bromide, giving an Et_2O -sol. Mg compound, the yield of (III) being 40–55%. In method (c) (I) and also an oil (IV), both containing Mg pyridyl bromide in some form, were isolated; (IV) is considered to be a complex of (I) where *n* is small with $MgEtBr$. Variability in yields and analyses is attributed to varying vals. of *n* and different proportions of (I) and (IV) (cf. Grignard, A., 1934, 909; Urien, *ibid.*, 640). The reaction may also be applied to 3-bromopyridine. R. G.

Thiocarbimide reaction and the structure of gelatin. O. HUPPERT (Collegium, 1937, 626–633).—Thiogelatin (cf. A., 1907, i, 740) is prepared (1) by hydrolysing gelatin with lime, treating with CS_2 , and oxidising, and (2) by treating it with CS_2 , then with pancreatin, and afterwards oxidising. The mechanism of the reactions has been studied: they can only give identical end products if gelatin is a polypeptide in which diketopiperazine rings are completed by means of residual valencies. Thiogelatin is considered to be the disulphide of a 5-substituted 2-thiohydantoin-gelatose. D. P.

Transformation of collagen into collagen II and gelatin. E. CHERBULEZ and K. H. MEYER (Compt. rend. Trav. Lab. Carlsberg, 1938, 22, 118–124).—When collagen (fibres from tendon of Achilles in the pig) is immersed for 45 sec. in H_2O at 62° there

is a reversible change (accompanied by contraction) from a substance containing crystallites into an amorphous product, collagen II. This is attacked by trypsin. If the amorphous material is carefully stretched under ice- H_2O , the fibres revert almost to the original length, and action of trypsin is considerably decreased. $HCO\cdot NH_2$ at 37° has a similar action to H_2O at 62°. When tendons are placed in 2% NaOH for several weeks, no elongation but pronounced swelling takes place, and the product is rapidly attacked by trypsin. Heating the swollen fibres to 50–60° causes rapid contraction and partial liquefaction, the liquid, on cooling, setting to a jelly characteristic of gelatin. J. N. A.

Amino-acid composition of zein. H. B. VICKERY (Compt. rend. Trav. Lab. Carlsberg, 1938, 22, 519–527).—1.6% of arginine and 0.77% of histidine have been isolated from zein. Lysine has not been obtained. J. N. A.

Electric furnace for automatic combustion in micro-elementary analysis. L. T. HALLETT (Ind. Eng. Chem. [Anal.], 1938, 10, 101–103).—An apparatus using electric furnaces of new design for the automatic combustion of micro-samples is described. The Al alloy furnaces are of the split type and can be easily removed from the combustion tube for cooling. The application of this type of furnace to determinations of C, H, N, halogen, and S is described. The no. of determinations per 8-hr. day is increased by 25%. L. S. T.

Micro-titrimetric dry combustion method for carbon. R. B. SCHMITT and J. B. NIEDERL (Mikrochem., 1938, 24, 59–64).—A method which combines dry combustion in the usual manner with titration of the CO_2 by means of standard $Ba(OH)_2$ is described. O. J. W.

Determination of carbon and hydrogen. F. B. STRAUSS (Chem. and Ind., 1938, 242).—Errors in micro- and semi-micro-determinations of C and H are overcome by a definite arrangement of absorbents in the cleaning apparatus and absorption tubes, and by only partly filling the combustion tube. O. M.

Micro-technique of organic qualitative analysis. D. G. FOULKE and F. SCHNEIDER (Ind. Eng. Chem. [Anal.], 1938, 10, 104–107).—Methods available for the preliminary examination of org. substances and the determination of physical consts. on the micro-scale are summarised. A micro-technique for detecting N, S, and halogens, based on the macro-method of Baker and Barkenbus (A., 1937, II, 222), is described. A capillary method and a Schlieren method for solubility have also been developed. L. S. T.

Micro-analytical determination of oxygen in organic compounds. J. UNTERZAUCHER and K. BÜRGER (Ber., 1938, 71, [B], 429–442).—The determination depends on the reactions, $CO + 3H_2 = CH_4 + H_2O$ and $CO_2 + 4H_2 = CH_4 + 2H_2O$. The catalyst is obtained by converting $Ni(NO_3)_2 \cdot 6H_2O$ by an excess of pure HCO_2H into $(HCO_2)_2Ni$ which is mixed with 10% of $(HCO_2)_4Th$ and heated at 130°, whereby ThO_2 is formed. The mixture is readily reduced *in situ* by H_2 . The SiO_2 tube contains

successively the boat with substance, a stopper, small platinised SiO_2 fragments (I) to ensure complete decomp. of the material, Ag stopper, CaO to absorb halogen (this is the only satisfactory medium but necessitates the introduction of a correction for the H_2O produced), a Ni wire spiral roughened by HNO_3 to remove S, Ag stopper, and the catalyst (II). The parts of the tube surrounding (I) and (II) are heated in electric furnaces at $1000\text{--}1100^\circ$ and $300\text{--}320^\circ$, respectively, and the intermediate portion of the tube is maintained at $600\text{--}700^\circ$ by a small burner. The H_2 is passed successively over P_2O_5 -pumice, red-hot Cu, and P_2O_5 -pumice. The usual absorbents for H_2O [CaCl_2 , $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, and CaSO_4] are inadmissible by reason of the frequent presence of NH_3 , and the customary open tube is useless. CaO in a specially designed tube attached to the main apparatus by ground-glass joints is satisfactory. H. W.

Modifications of the Kjeldahl method. J. MILBAUER (Z. anal. Chem., 1938, 111, 397—407).—The times required for the combustion of sucrose by H_2SO_4 at 302° and at the b.p. in presence of Se, HgO , CuSO_4 , Te, Au, V_2O_5 , Pt, Sb_2O_3 , Pd, Ag_2SO_4 , As_2O_3 , and NiSO_4 as catalysts are recorded. At the b.p. of the H_2SO_4 the order of decreasing efficiency is that given, but for 302° the order is changed, with Se still the most effective single catalyst. Data for mixtures in pairs of SeO_2 , HgSO_4 , CuO , Ag_2SO_4 , and TeO_2 in different proportions are also given. The most effective mixture is $\text{SeO}_2 + \text{HgSO}_4$ (Se : Hg = 1 : 4). Times required by numerous catalysts etc. recommended in the literature have also been determined. Air-stirring generally reduces this time. For the kjeldahlisation of NHPh_2 Milbauer's method (A., 1937, I, 425) using a catalyst of $\text{HgO} + \text{SeO}_2 + \text{P}_2\text{O}_5$ effects the quickest conversion. L. S. T.

Determination of sulphur in organic materials. F. W. KLINGSTEDT (Z. anal. Chem., 1938, 112, 101—103).—1—5 g. of the substance in a fairly short-necked Kjeldahl flask is moistened with 5—10 c.c. of conc. HNO_3 , 0.5—1.0 g. of MgO is added, and finally 15—20 c.c. of fuming HCl are poured in. The flask is heated gently for 2—4 hr. with a funnel in its mouth. When oxidation is complete the solution is evaporated to dryness and the residue heated until white. 10 c.c. of conc. HCl are added and the material is again evaporated to dryness. The residue is dissolved in HCl and the SO_4^{2-} determined as BaSO_4 . Examples are given of the application of the method to analysis of sulphite pulp and sawdust, and to waste- H_2O from a sulphite-cellulose factory. J. W. S.

Determination of halogens in organic compounds. E. WALTER (Chem. Fabr., 1938, 11, 140—141).—The substance, mixed with Hg_2SO_4 , is decomposed by conc. $\text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$ at 150° . Cl_2 or Br liberated is absorbed in alkaline K_2SO_3 . I is left in the reaction product as HIO_3 and may be determined after reduction. The halogens in the absorbate may be determined gravimetrically or titrimetrically. The apparatus is figured. R. S. B.

Direct volumetric micro-determination of halogens in organic substances. (Hydrogenation method.) A. LACOURT (Mikrochem., 1938,

23, 308—325).—The product obtained from $\text{Ni}(\text{CrO}_2)_2$ [prep. by heating $\text{NiCrO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$] by reduction in HCl gas at 110° is a good hydrogenation catalyst. The org. material under analysis is distilled in a current of H_2 over the catalyst heated at $400\text{--}450^\circ$. The HCl , HBr , or HI produced is absorbed in H_2O and titrated with NaOH or NaBO_2 , using Me-orange or Me-red as indicator. In absence of N, Cl, Br, and I can be determined in a few min. using 2—5-mg. samples. J. W. S.

Micro-determination of halogen by combustion.—See A., 1938, I, 279.

Determination of unsaturation in organic compounds. H. J. LUCAS and D. PRESSMAN (Ind. Eng. Chem. [Anal.], 1938, 10, 140—142).—Under the conditions stipulated by Frieman *et al.* (A., 1937, I, 313) several alkenes and alkenes react quantitatively with Br in the presence of HgSO_4 . Δ^a -Pentene, -hexene, -heptene, and -hexene, Δ^b -heptene, CPh:CH , cyclohexene, and $(\text{CHCl})_2$ react rapidly, maleic and fumaric acids react more slowly, whilst $\text{CH}_2\text{C}=\text{CO}_2\text{H}$, $\text{CHPh:CH}=\text{CO}_2\text{H}$ and $(\text{CMe:CH}_2)_2$ undergo substitution as well as addition. F. N. W.

Semi-micro-determination of acetyl. K. W. MERZ and K. G. KREBS (Ber., 1938, 71, [B], 302—305).—The following modifications of the method of Kuhn and Roth are recommended for the determination of acyl in sensitive org. compounds. The compound (20—40 mg.) is hydrolysed in Kuhn's apparatus with 15 c.c. of 25% $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{SO}_3\text{H}$ (duration for O- and N-acyl compounds up to 30 min. and 180 min., respectively). Air or N_2 is passed through the apparatus. After complete hydrolysis the condenser is rinsed with 5—10 c.c. of H_2O and reversed. The org. acid is distilled off with occasional replacement of the distillate by an equal vol. of H_2O ; the process is continued until a further 6—7 c.c. of distillate do not require more than 0.05—0.08 c.c. of 0.02N-NaOH. Alternatively the compound (20—40 mg.) is hydrolysed by 10 c.c. of N-KOH to which 10 c.c. of H_2O are added, replaced, if necessary, by abs. acid-free MeOH (duration for O- and N-acyl, 15 min. and 45—60 min., respectively). The condenser is rinsed with 5 c.c. of H_2O , and MeOH, if used, must be distilled from the solution before acidification. The required amount of conc. H_3PO_4 or solid $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{SO}_3\text{H}$ is added and the volatile org. acid is distilled and titrated as described above. H. W.

Microchemical technique. II. Modification of the micromethoxyl apparatus to the Vieböck procedure. M. LIEFF, C. MARKS, and G. F. WRIGHT (Canad. J. Res., 1937, 15, B, 529—531).—An absorbing chamber for the Vieböck-Pregl micro-OMe determination is described. A. LI.

Determination of ethylene glycol nitrate in air. V. ÖHMAN and G. LAURENT (Svensk Kem. Tidskr., 1938, 50, 38—42).— <2 mg. of $(\text{CH}_2\text{O} \cdot \text{NO}_2)_2$ per cu.m. of air is determined by passing through glass beads moistened with $\text{OH} \cdot \text{C}_6\text{H}_5(\text{SO}_3\text{H})_2$ in H_2SO_4 (to liberate HNO_3), diluting with H_2O , adding NH_3 , and matching colorimetrically against a standard solution, prepared from KNO_3 . Org. matter, dust, etc. must be excluded. A blank is necessary. R. S. C.

Determination of glycerol and ethylene glycol by the acetin method. V. ÖHMAN and G. LAURENT (Svensk Kem. Tidskr., 1938, 50, 35—37).—Glycerol and $(\text{CH}_2\text{OH})_2$ are determined by heating at 100° with 12% $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ for 60 and 10 min., respectively, diluting with H_2O , and titrating the AcOH with NaOH (cresolphthalein). A blank is necessary. The results agree with those obtained by the chromate method. R. S. C.

Determination of glycerol. R. CUTHILL and C. ATKINS (J.S.C.I., 1938, 57, 89—91).—Glycerol (I) may be determined in aq. solution by boiling with excess of standard $\text{Ce}(\text{SO}_4)_2$ solution, then titrating back the excess with standard $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$. Each mol. of (I) reacts with 4 O. Alternatively the (I) may be boiled with a small excess of standard alkaline solution of Br, which oxidises the (I) quantitatively to CO_2 and H_2O : $\text{C}_3\text{H}_5(\text{OH})_3 + 7\text{O} = 4\text{H}_2\text{O} + 3\text{CO}_2$; the excess of OBr^{\cdot} is determined by adding KI and titrating with $\text{Na}_2\text{S}_2\text{O}_3$. R. C.

Reactivity of formic acid. Method of determining side-chain halogen in aromatic compounds. (Miss) K. D. GAVANKAR, L. S. HEBLE, and T. S. WHEELER (J. Univ. Bombay, 1937, 6, Part II, 112—113).—The compound is heated with HCO_2Na in anhyd. HCO_2H and poured into AgNO_3 , and the halogen determined as Ag halide. F. R. S.

Determination of the mol. wt. of higher, monobasic fatty acids. G. LODE (Österr. Chem.-Ztg., 1938, 41, 95—101).—Pure or mixed fatty acids are determined by means of the Zn, UO_2 , or less well, Cu salts, which are prepared by mixing the acid and metal acetate in EtOH , adding to H_2O , and igniting the ppt. Other salts are less suitable. R. S. C.

Detection and determination of fumaric acid in presence of maleic, itaconic, citraconic, *cis*- and *trans*-aconitic acids. G. SEMERANO (Mikrochem., 1938, 24, 10—15).—Fumaric acid (I) can be detected in presence of the above-mentioned acids by means of the polarograph, using the Li salts in 0.1N-LiCl. If the proportion of (I) is not too small, especially with respect to the amount of *trans*-aconitic acid, it can be determined by this method in the absence of other substances having reduction potentials only slightly < the deposition potential of Li^{\cdot} . O. J. W.

Potentiometric titration [of organic acids] in non-aqueous solutions.—See A., 1938, 1, 266.

Some limitations of 2:4-dinitrophenylhydrazine as a reagent for carbonyl groups. C. F. H. ALLEN and J. H. RICHMOND (J. Org. Chem., 1937, 2, 222—226).—The use of HCl instead of H_2SO_4 in the prep. of 2:4-dinitrophenylhydrazones of carbonyl compounds is recommended since traces of the latter persist through several recrystallisations and may lead to difficulties if secondary reactions are possible. A slight excess of the carbonyl compound avoids difficulties due to the unused reagent which is difficult to separate. Purification is best accomplished with EtOH , dioxan, aromatic hydrocarbons, or esters; CHCl_3 gives unsatisfactory separation of mixtures. The derivative should be recryst. to the same const. m.p. from two different solvents. Unsaturated

ketones may give rise to mixtures: benzylideneacetophenone (I) readily gives a mixture containing the pyrazoline derivative. The 2:4-dinitrophenylhydrazones of the following have been prepared; m.p. are given in parentheses and are corr. Hydrocinnamaldehyde (149°); $\text{CPh}:\text{C}:\text{CHO}$ (190°); COPr^{a} (88°); COBu^{a} (66°); hexadecane-2:15-dione (117°); 3-methylcyclohexanone (155°); $\text{CO}(\text{CH}_2\text{Ph})_2$ (100°); *p*- $\text{C}_6\text{H}_4\text{Cl}:\text{COMe}$ (231°); *p*- $\text{C}_6\text{H}_4\text{Br}:\text{COMe}$ (230°); *p*- $\text{C}_6\text{H}_4\text{Me}:\text{COMe}$ (248°); *p*- $\text{OMe}:\text{C}_6\text{H}_4:\text{COMe}$ (220°); phenacyl chloride (212°); benzylacetophenone (180°); vanillylideneacetone, (230°); Et benzoylformate (158°); (I) (245°); deoxybenzoin (204°). The pyrazoline from (I) has m.p. 175° . H. G. M.

Colorimetric determination of cysteine and cystine with phosphotungstic acid. A. SCHÖBERL and P. RAMBACHER (Biochem. Z., 1938, 295, 377—390; cf. A., 1937, II, 328).—A photometric method dependent of the use of phosphotungstic acid (I) is described. Const. temp. (e.g., 20°) must be maintained during the determination. In presence of cysteine or cystine Na_2SO_3 does not reduce (I).

W. McC.

Determination of glycocyclamine and of arginine.—See A., 1938, III, 454.

Gasometric determination of carboxyl groups in amino-acids. D. D. VAN SLYKE and R. T. DILLON (Compt. rend. Trav. Lab. Carlsberg, 1938, 22, 480—486).—The method depends on the reaction of NH_2 -acids with ninhydrin (I), when 1 mol. of CO_2 is evolved, which is determined in the apparatus described by Van Slyke *et al.* (A., 1933, 1314). Isatin can be used in place of (I), but reaction is slower. Reaction is quant. with all types of NH_2 -acids obtained by protein hydrolysis except with aspartic acid, which evolves 1.9 mols., and glutamic acid which evolves 1.03 mols., of CO_2 . Lysine quantitatively gives 1 mol. of CO_2 but this is followed by a slow evolution of more CO_2 . Proline and hydroxyproline react like NH_2 -acids. Org. acids and $\text{CO}(\text{NH}_2)_2$ do not react. Peptides yield no CO_2 even from the $\cdot\text{CO}_2\text{H}$. If $\cdot\text{NH}_2$ be removed from α - to β - or γ -position, reactivity of $\cdot\text{CO}_2\text{H}$ diminishes. Esters, amides, and acids having no H on the $\text{NH}_2\text{-N}$ do not react.

J. N. A.

Colorimetric test for detection of *p*-hydroxybenzoic acid in presence of salicylic acid. S. G. STEVENSON and J. C. L. RESUGGAN (Analyst, 1938, 63, 152—155).—Under certain conditions *p*- $\text{OH}:\text{C}_6\text{H}_4:\text{CO}_2\text{H}$ (I) couples with solutions of benzenediazonium salts to give a dark, red-brown mixture of mono-, bis-, and tris-azophenols, the acid being decarboxylated, whereas salicylic acid (II) couples without decarboxylation and the product is consequently sol. in alkalis. Use is made of this distinction in a colour reaction for (I) which is sensitive to 1 in 50,000 either in presence or absence of (II). (Cf. A., 1937, II, 268.) E. C. S.

Determination of terpineol in its aqueous solutions by a surface tension method. V. I. VARENTZEV (J. Appl. Chem. Russ., 1938, 11, 142—146).—The terpineol content of aq. solutions is derived from the surface tension-concn. curve, at 20° .

R. T.

Determination of tannin. H. TRETZMÜLLER (Mitt. tech. Versuchsamtes, 1935, 24, 77—78; Chem. Zentr., 1936, i, 4949).—A 0.5% solution of tannin-blue RB in 1% tartaric acid is titrated with the tannin solution (0.1—0.2%) until the dye is completely pptd. as lake. J. S. A.

Precipitation of alkaloids with sodium glycerophosphate. L. ROSENTHALER (Sci. pharm., 1935, 6, 122—123; Chem. Zentr., 1936, ii, 346—347).—The character of the ppts. given with Na glycerophosphate by berberine, brucine, quinine, cinchonidine, cinchonine, diocaine, heroin, caffeine, cocaine, morphine, nycaine, percaïne, eserine, and strychnine is described. H. N. R.

New colour reactions of barbiturates. M. PESEZ (J. Pharm. Chim., 1938, [viii], 27, 247—254).—MeCHO, CHO·CO₂H, CCl₃·CHO, (CHO)₂, furfuraldehyde, hydroxymethylfurfuraldehyde, and PhCHO do not give the colour reaction of vanillin with conc. H₂SO₄ and diallylbarbituric acid (I). (I) with conc. H₂SO₄ and 40% CH₂O at 100° gives an orange-yellow colour and a green fluorescence which persists on dilution. *iso*Propyl- and *isobutyl*-allylbarbituric acid give similar reactions. Phenyl- and *N*-methylphenyl-ethylbarbituric acid (II) give an intense red colour which distinguishes them from veronal. (I) with *p*-NMe₂·C₆H₄·CHO and conc. H₂SO₄ affords a pink colour changed to red at 100° and to reddish-purple with a little H₂O; the reaction is characteristic of the presence of two allyl groups in the mol. *o*-OH·C₆H₄·CHO gives an analogous reaction, sp. for (I). Barbiturates with Ph as a substituent with conc. H₂SO₄-conc. HNO₃ afford (NO₂)₂-derivatives which with COMe₂ and alkali give violet compounds sol. in COMe₂. With a less intense nitrating reaction, (II) is distinguished from other similar barbiturates by the yellow to violet colours it gives depending on the conditions. J. L. D.

Determination of quinine salts in presence of methylene-blue. J. G. SOBRINHO (Boll. Chim. farm., 1938, 77, 145—148).—Normal gravimetric and volumetric methods are not applicable to quinine salts in presence of methylene-blue. The method recommended is to ppt. the alkaloid (together with absorbed methylene-blue) with silicotungstic acid, and ash the ppt. at 1000° to const. wt. which, $\times 0.227$, = quinine. F. O. H.

Two new reagents which differentiate morphine from oxydimorphine. M. PESEZ (J. Pharm. Chim., 1938, [viii], 27, 255—262; cf. A., 1937, II, 478).—Oxydimorphine (<0.1 g.) (I) with conc. HCl-*p*-NMe₂·C₆H₄·CHO at 100° affords an emerald-green colour. Morphine (<0.01 g.) (II), codeine, dionin, peronin, and heroin give a red colour. If conc. H₂SO₄ is substituted for conc. HCl, (I) and (II) (<1 mg. in each case) at 100° give green and reddish-brown colours, respectively, which are modified differently by H₂O and aq. NH₃. Warm aq. 5% H₂C₂O₄ with HgCl₂ and Al or with H₂SO₄-CuSO₄-Zn affords a solution of CHO·CO₂H which with conc. H₂SO₄ and (I) (0.1—0.2 mg.) at 100° gives an emerald-green colour, modified by H₂O and aq. NH₃. The reaction

is characteristic of (I). H₃PO₄ substituted for H₂SO₄ gives at 100° a green and then a reddish-brown colour. J. L. D.

Action of ninhydrin, alloxan, and isatin on amino-acids and polypeptides. R. ABDERHALDEN (Z. physiol. Chem., 1938, 252, 81—94; cf. Ruhemann, J.C.S., 1911, 99, 792, 1486).—Alloxan (I) and ninhydrin (II) at room temp. and isatin at higher temp. eliminate NH₂ from NH₂-acids (not glycine, serine, cystine, or histidine), converting them into the corresponding aldehydes having 1 C less. The aldehydes are identified by conversion into compounds with dimethylcyclohexanecione. Glutamic acid gives the succinaldehyde compound, m.p. 246°, and isatide (2 : 4-dinitrophenylhydrazone, m.p. 202—203°). The compounds with EtCHO, Pr^oCHO, Pr^βCHO, Bu^oCHO, Bu^βCHO, CHMeEt·CHO, and CH₂Ph·CHO have m.p. 156°, 134—135°, 153—154°, 107—108°, 157°, 135—136°, and 164°, respectively. The colours given by NH₂-acids with (I) and (II) [proline gives no colour with (I) and only a weak yellow colour with (II)] differ in intensity and in rate of development and disappearance but the order of intensity is the same with both compounds. Ascorbic acid, at room temp., reduces (I) to alloxantin and (II) to hydrindantin. At room temp. colours are produced by (I) and (II) with polypeptides usually only when they contain a glycine residue with free ·NH₂. (II) is converted by alanine, leucine, glycine, and glutamic acid into hydrindantin and (I) by glycine, alanine, α-aminobutyric acid, and valine into compounds of unknown constitution. W. McC.

Analysis of proteins. X. Examination of Van Slyke's method, and determination of tryptophan by bromination. R. H. A. PLIMMER and J. LOWNDES (Compt. rend. Trav. Lab. Carlsberg, 1938, 22, 434—440; cf. A., 1937, III, 457).—Determination of NH₂-N has been improved by use of 2·8N-HCl instead of AcOH and good results with lysine in the Van Slyke fraction after removal of histidine, arginine, and cystine have been obtained in a reaction time of 25—30 min. without shaking, followed by 5 min. shaking at 11°. Histidine cannot be determined by direct bromination as too high results are obtained. Tyrosine is determined by the method of Folin and Ciocalteu (A., 1927, 892) in the (NH₂)₁-fraction of Van Slyke's method. Determination of tryptophan by bromination gives the same results as the colorimetric method of Folin *et al.* Serine evolves considerable amounts of NH₃ when boiled with 20% NaOH for 6—7 hr., whilst *isoserine*, hydroxyproline, and hydroxyaspartic acid yield only small amounts. J. N. A.

Modification of the Van Slyke method of analysing proteins. E. MARIOTTI (Atti R. Accad. Lincei, 1937, [vi], 26, 238—242).—Basic Pb hydroxide is a convenient reagent; it completely liberates NH₃ from its salts, has practically no action on arginine, even at 100°, and with cystine gives NH₃ and PbS (92% theoretical). In this way (applying a correction), cystine can be determined in a mixture to ± 2 —3%, and the phosphotungstate determination of NH₂-acids is not impeded. An analytical routine is described. E. W. W.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JUNE, 1938.

Electrochemical synthesis of organic compounds. N. N. MELNIKOV (Uspechi Chim., 1937, 6, 4—41).—A review.

R. T.

Asymmetric synthesis. R. BOUSSET (Bull. Soc. chim., 1938, [v], 5, 479—493).—Theoretical. If a racemic substance, *A*, yields *B* by the agency of, or combination with, an active substance which is regenerated unchanged, and the activity and yield of *B* are such that *B* would be active even if all material unaccounted for had been of opposite rotation, then an asymmetric synthesis will have been achieved. Known reactions, *e.g.*, of bacteria, Kuhn's and McKenzie's reactions, are merely resolutions.

R. S. C.

Purification and characterisation of substances of high mol. wt. A. TISELIUS (Svensk Kem. Tidskr., 1938, 50, 58—68).—A review with special reference to electrophoretic methods.

A. LI.

Decomposition of hydrocarbons.—See A., 1938, I, 330.

Methylene. T. G. PEARSON, R. H. PURCELL, and G. S. SAIGH (J.C.S., 1938, 409—424).—Decomp. of keten by light (cold Hg arc), and of CH_2N_2 by heat (400°) or by light, yields CH_2 , detected by combination with Te (at 70°) or Se mirrors. Gaseous CH_2Te and CH_2Se are formed, and polymerise in small yield on cooling to two solids in each case. In presence of CH_2N_2 , CH_2 has a half-val. period of 5×10^{-3} sec., but in pure keten it shows no measurable decay in 50×10^{-3} sec. Its stability in CH_2N_2 is increased by dilution with keten, Et_2O , or N_2 . CH_2 behaves as a reactive mol. rather than a free radical, and undergoes a bimol. reaction with CH_2N_2 . Measurements of the rate of removal of mirrors by CH_2 from CH_2N_2 heated at different temp. show the activation energy in the production of CH_2 to be 22 kg.-cal.

A. LI.

[Rates of] condensation of ethane, propane, butane, and propylene.—See A., 1938, I, 317.

Polymerisation of unsaturated hydrocarbons. H. I. WATERMAN and J. J. LEENDERTSE (J. Inst. Petroleum Tech., 1938, 24, 16—37).—Aliphatic olefines (C_2 — C_{16}) and cyclic unsaturated hydrocarbons (pinene, cyclohexene, and tetrahydronaphthalene) were polymerised with AlCl_3 , and in a few cases with BF_3 or Al_2O_3 , at -78° to 70° . Polymerisation products were fractionated and hydrogenated and the fractions then examined for cyclisation by the sp. refraction-mol. wt. method. Some ring formation was evident in every case except with hexadecene. When polymerising cyclic unsaturated

hydrocarbons ring-opening was observed in some cases. By varying the base material and conditions practically any desired composition can be obtained.

By comparing the composition of saturated hydrocarbon mixtures as derived from sp. refraction and sp. parachor (based on at. parachors of Mumford and Phillips) a qual. idea of the degree of branching of the hydrocarbon mixtures can be obtained, particularly of aliphatic hydrocarbon mixtures. The sp. parachor-mol. wt. method gives information as to the degree of cyclisation, but the sp. parachor is also dependent on the branching of the mol. The difference between the no. of rings calc. from the parachor and the true no. of rings found by the sp. refraction-mol. wt. method gives an indication of the amount of branching in the saturated hydrocarbons.

C. C.

Addition of hydrogen chloride to butadiene. M. S. KHARASCH, J. KRITCHEVSKY, and F. R. MAYO (J. Org. Chem., 1938, 2, 489—496).—At -80° or 25° HCl and butadiene alone give 35% or in AcOH 50—80% of a mixture containing 75—80% of $\text{CH}_2\text{:CH}\cdot\text{CHMeCl}$ (I), b.p. $64^\circ/750$ mm., and 25—20% of $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ (II), b.p. $84^\circ/750$ mm., but no $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$. Anhyd. FeCl_3 rapidly rearranges (I) or (II) to a 1:1 mixture. H_2O and peroxides are without effect. 1 mol. of HCl slowly gives a mixture containing 70—75% of (I) and 30—25% of (II); FeCl_3 -HCl gives the same mixture much more rapidly. At 100° more (II) is formed. At -80° HCl alone has practically no effect. CuCl -HCl also catalyses the change. It is concluded that the mixture obtained from butadiene and HCl is not determined by isomerisation. Similarly the products obtained by HBr under anaerobic conditions are a primary mixture; the effect of peroxides or HBr is to isomerise this mixture.

R. S. C.

Thermal polymerisation of butadiene.—See A., 1938, I, 315.

Conjugated systems. IV. Reactions of divinyl with hypochlorous acid and its esters. V. Reactions of divinyl with hypobromous acid and with alkyl hypobromites. A. A. PETROV (J. Gen. Chem. Russ., 1938, 8, 131—141, 142—150).—IV. Divinyl (I) at -12° and 10% aq. $\text{NH}_2\cdot\text{CO}\cdot\text{NHCl}$ yield α -chloro- β -hydroxy- Δ^7 -butene (II), b.p. 144 — 147° , (acetate, b.p. 163 — 166°), converted by heating with aq. KOH into divinyl α -oxide (III), from which γ -hydroxy- δ -methoxy-, b.p. 143 — 144° (acetate, b.p. 159 — 162°), - δ -ethoxy-, b.p. 153 — 157° , or - δ -isobutoxy- Δ^8 -butene, b.p. 173 — 180° , are obtained by boiling with the appropriate alcohol. (II) and Br in CHCl_3 yield α -chloro- γ - δ -dibromo- β -hydroxybutane, b.p. 129 —

130°, oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in dil. H_2SO_4 to α -chloro- $\gamma\delta$ -dibromo- β -ketobutane, b.p. 132—133°. (I) when shaken with EtOH and $\text{PhSO}_2\text{NCl}_2$ yields α -chloro- β -ethoxy- Δ^2 -butene, b.p. 137.5—138.5°, which, with Br in CHCl_3 , gives α -chloro- $\gamma\delta$ -dibromo- β -ethoxybutane, b.p. 114—115°/10 mm.

V. (I) and aq. NHAcBr give α -bromo- β -hydroxy- Δ^2 -butene, b.p. 161—162.5° (acetate, b.p. 72°/10 mm.), which yields (III) as above, and with Br in CHCl_3 at -10° gives $\alpha\gamma\delta$ -tribromo- β -hydroxybutane, b.p. 141—141.5°/10 mm. (acetate, b.p. 146°/10 mm.); this is oxidised to $\alpha\gamma\delta$ -tribromo- β -ketobutane, b.p. 121°/10 mm.

R. T.

Isomerisation of diallyl. J. M. SLOBODIN (J. Gen. Chem. Russ., 1938, 8, 188—189).—Levina's conclusion that Al_2O_3 is a more active catalyst of isomerisation of diallyl than is floridin (A., 1938, II, 48) is questioned.

R. T.

Spectrographic and chemical study of some aliphatic terpenes. III. *allo*Ocimene and [its] hydrogenation products. G. DUPONT, R. DULOU, V. DESREUX, and R. PICOUX. IV. *Ocimene*. G. DUPONT and V. DESREUX (Bull. Soc. chim., 1938, [v], 5, 322—336, 337—339; cf. A., 1937, II, 200; 1938, II, 80).—III. When prepared by pyrolysis of pinene (A., 1935, 1127) *allo*ocimene (I) consists of $\beta\zeta$ -dimethyl- $\Delta^{8\alpha}$ -octatriene (cf. A., 1917, i, 111), with no significant amount of the isomeric $\Delta^{8\eta}$ -compound. This is shown by the Raman spectrum (which is discussed), by the formation of a single compound, m.p. 81—82°, with maleic anhydride (II), and by the following reactions. With O_2 - O_3 , (I) gives COMe_2 , HCO_2H , $\text{H}_2\text{C}_2\text{O}_4$, Ac_2 , and $\text{OH}\cdot\text{CHMe}\cdot\text{COMe}$, and not CH_2O or AcOH . Reduction of (I) gives mixed products, except with Na-NH_3 , which yields $\beta\zeta$ -dimethyl- Δ^8 -octadiene (III), b.p. 57—58°/12 mm., shown by Raman spectrum to be homogeneous. This with (II) gives a 3-methyl-3-ethyl-6-isopropyl- $\Delta^{1,5}$ -tetrahydrophthalic acid, m.p. 158—160°, and a compound, b.p. 112—115°/12 mm., with $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$. Further reduction of (III) by H_2 -Ni gives trans- $\beta\zeta$ -dimethyl- Δ^8 -octene, b.p. 45—46°/12 mm.; using Na-NH_3 , the *cis*-form is also obtained. Reduction of (I) by Na-EtOH yields an equal mixture of (III) with $\beta\zeta$ -dimethyl- $\Delta^{8\epsilon}$ -octadiene (IV), b.p. 59—59.5°/12 mm., of which the structure is established by the Raman spectrum, and by ozonolysis to COMe_2 and COMeEt ; with H_2 -Ni (III) in the mixture is hydrogenated and (IV) remains unchanged. With H_2 -Ni at room temp., (I) gives a mixture of $\beta\zeta$ -dimethyl- Δ^8 with some Δ^8 -octene (ozonised). Using H_2 -Pt, a similar product is obtained.

IV. From its Raman spectrum, and its reduction by Na-EtOH to dihydromyrcene (A., 1937, II, 27), *ocimene* is regarded not as a $\Delta^{8\eta}$ -compound (A., 1926, 619) but as $\beta\zeta$ -dimethyl- $\Delta^{8\eta}$ -octatriene.

E. W. W.

Photodecomposition of methyl and ethyl iodides.—See A., 1938, I, 318.

Allylic rearrangements. VII. Action of metals on crotyl and methylvinylcarbinyl bromides. W. G. YOUNG, N. KAUFMAN, A. LOSHOKOV, and D. PRESSMAN (J. Amer. Chem. Soc., 1938, 60,

900—903; cf. A., 1938, II, 2).—Identical products are obtained by treating $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ or $\text{CH}_2\cdot\text{CH}\cdot\text{CHMeBr}$ with metals in 80% EtOH. For Al-Hg, Zn, Cr, Cd, and Sn the yield (41—96%) of Δ^8 -butene \propto the mol. reduction potential of the metal, the bivalent metals and Cr-Al forming distinct series. The ratio, *cis* : *trans*- Δ^8 -butene (1.2—5.6), of the product \propto the mol. reduction potential independently of the valency. Equilibration is due to equilibration of the organometallic halide or to resonance between $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2^+$ and $\text{CH}_2\cdot\text{CH}\cdot\text{CHMe}^+$ at the moment of reaction with the metal.

R. S. C.

Effect of groups on reaction rate. Reaction of $\alpha\beta$ -dibromides with sodium iodide. T. L. DAVIS and R. HEGGIE (J. Org. Chem., 1938, 2, 470—479).—The reaction of 0.3M-NaBr with 0.015M-(CH_2Br)₂, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{OH}$, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ (I), $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$, $\text{CHMeBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, and *trans*-($\text{CHBr}\cdot\text{CO}_2\text{H}$)₂ in EtOH, usually at 25.3°, 37.2°, and 56.3°, and with $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{X}$ (X = H, *p*-NO₂, and *m*-Cl), $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{COMe}$, and (I) in COMe_2 at suitable temp. between 0° and 25.3°, gives good *k* for second order or ψ -unimol. reactions. $\text{CHMeBr}\cdot\text{CH}_2\text{Br}$ and $\text{CHPrBr}\cdot\text{CH}_2\text{Br}$ do not give good *k*. Using second-order *k*, *E* and *P* are calc. from the relation, $k = PZe^{-E/RT}$, *Z* being taken as 2×10^{11} . *P* may be $\gg 1$ and so needs liberal interpretation. Me, Pr, and $\text{CH}_2\cdot\text{OH}$ increase *E*; (CO_2H)₂ and $\text{CO}_2\text{Et} > \text{CO}_2\text{H}$ decrease *E*; the effect of CO_2H is $>$ that of Me. A CO_2H reduces *P*, but a second CO_2H partly restores it. *COPh* greatly increases *k*. Reaction of (I) is much faster in COMe_2 than in EtOH. Individual results are further discussed.

R. S. C.

Stereoisomerides of $\alpha\beta$ -dichloro- $\alpha\beta$ -dibromoethylene. H. VAN DE WALLE and J. PENS (Bull. Soc. chim. Belg., 1938, 47, 217—220).—*trans*- $\alpha\beta$ -Dichloro- $\alpha\beta$ -dibromoethylene, m.p. -12.2° , b.p. 165°, easily polymerised, prepared by refluxing (CClBr)₂ with Zn-EtOH for 20 hr., is much less stable to KOEt (10 min.) than the *cis*-form (cf. A., 1921, i, 491); the latter is obtained from KOEt and $\text{CHBr}_2\cdot\text{CCl}_2\text{Br}$.

A. T. P.

Detection of methyl alcohol. E. EEGRIWE (Mikrochim. Acta, 1938, 2, 329—331).—A drop of the solution to be tested is acidified with 0.05 c.c. of 5% H_3PO_4 and about 0.065 c.c. of 5% KMnO_4 is added. After 1 min. finely powdered solid NaHSO_3 is added slowly until the solution is colourless, and 4 c.c. of H_2SO_4 (150 c.c. of 96% H_2SO_4 to 100 c.c. of H_2O) are then added, together with finely ground chromotropic acid, and the solution is heated for 10 min. at 60°. A violet-pink colour is produced if the initial MeOH content of the drop is $< 3.5 \times 10^{-6}$ g. Org. compounds which are found not to affect the test are listed. 5.3×10^{-6} g. of MeOH can be detected in presence of 6.1×10^{-3} g. of EtOH.

J. W. S.

Allylic rearrangements. V. Mechanism of the reaction of crotyl alcohol and methylvinylcarbinol with solutions of hydrogen bromide. W. G. YOUNG and J. F. LANE (J. Amer. Chem. Soc., 1938, 60, 847—853; cf. A., 1937, II, 480).—Reaction of $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ and $\text{CH}_2\cdot\text{CH}\cdot\text{CHMe}\cdot\text{OH}$ with HBr is assumed to occur mainly by way of a resonant-

ing mixture of $\text{CHMe}:\text{CH}:\text{CH}_2^+$ and $\text{CH}_2:\text{CH}:\text{CHMe}^+$, which gives the equilibrium mixture of bromides, and to a smaller extent by direct replacement. The thermal equilibrium mixture of the bromides in 48% HBr at 25° with or without addition of H_2SO_4 is determined. The amounts of the alcohols reacting by each process are then determined from the results of Young and Lane (*loc. cit.*) and from new data for HBr-AcOH at 0°. 2.9–11.9% reacts by direct replacement. R. S. C.

Resolution of *n*-propylpropenylcarbinol. Refractivity and optical rotatory dispersion of substituted allyl alcohols. C. L. ARCS and J. KENYON (J.C.S., 1938, 312–318).—*dl-n*-Propylpropenylcarbinol (acetate, b.p. 63–64.5°/12 mm.; benzoate, b.p. 146°/12 mm.; Me ether, b.p. 135°/760 mm.) was resolved through the strychnine salt of its H phthalate. (+)-*n*-Propylpropenylcarbinyl H phthalate has m.p. 74–75°, $[\alpha]_{\text{D}}^{16} +22.85^\circ$ in EtOH ($[\alpha]$ for various λ in EtOH, C_6H_6 , CHCl_3 , and CS_2 at room temp. are recorded), and is hydrolysed (NaOH) with slight racemisation to the (+)-alcohol (I), b.p. 63.5°/15 mm., $\alpha_{\text{D}}^{16} +4.58^\circ$ (l, 0.5) [benzoate, b.p. 158°/16 mm., $\alpha_{\text{D}}^{16} +11.16^\circ$ (l, 0.5); acetate, b.p. 74°/16 mm., $\alpha_{\text{D}}^{21} -21.98^\circ$ (l, 0.5): vals. for other λ also given for both of these derivatives] (cf. A., 1934, 1088), which shows no mutarotation. Vals. for α of (–)-*n*-propylpropenylcarbinyl Me ether for various λ at 26°, and for α of (I) for various λ and temp., and for $[\alpha]$ in C_6H_6 , CHCl_3 , CS_2 , and $\text{C}_5\text{H}_5\text{N}$ for various λ at room temp. are recorded. Catalytic reduction of (I) and its esters gave optically inactive $\text{CHPr}^a:\text{OH}$ and its esters respectively, indicating the absence of the isomeride, $\text{CHPr}^a:\text{CH}:\text{CHMe}:\text{OH}$, and its esters. The $[R]_D$ and optical rotatory dispersion of (I) and the optically active forms of $\text{CHMe}:\text{CH}:\text{CHMe}:\text{OH}$, $\text{CHPh}:\text{CH}:\text{CHMe}:\text{OH}$, $\text{CHMe}:\text{CH}:\text{CHPh}:\text{OH}$, and $\text{CMe}_2:\text{CH}:\text{CHMe}:\text{OH}$ are compared. These alcohols are considered to have the *trans*-configuration. The rotatory dispersion of the alkylallyl alcohols in complex, but that of the phenylallyl alcohols is simple, and it is suggested that a large proportion of the rotatory power of the latter is due to induced dissymmetry of the Ph. H. G. M.

Preparation of anhydrous pinacol. K. A. KRASUKI and S. MAMEDOV (J. Gen. Chem. Russ., 1938, 8, 67–70).—The m.p. of anhyd. pinacol is 43°, and of the hexahydrate 45–46°; the lowest m.p. obtained for mixtures of the two is 29–30° (19% of hexahydrate). R. T.

Rate of hydrolysis of enol ethers.—See A., 1938, I, 316.

Synthesis of disodium phenyl phosphate. H. F. FREEMAN and C. W. COLVER (J. Amer. Chem. Soc., 1938, 60, 750–751).— POCl_2OPh [modified prep. in 70.4% yield with 8.2% of $\text{POCl}(\text{OPh})_2$], b.p. 240°, with H_2O , followed by Na_2CO_3 , gives a 68.2% yield of pure $\text{Na}_2\text{H}_2\text{P}_2\text{O}_4$. R. S. C.

Synthesis of 5-phospho-*d*-arabinose. P. A. LEVENE and C. C. CHRISTMAN (J. Biol. Chem., 1938, 123, 607–611).—Interaction of isopropylidene-*d*-arabinose and POCl_3 in $\text{C}_5\text{H}_5\text{N}$, followed by hydrolysis ($0.3\text{N-H}_2\text{SO}_4$), yields *d*-arabinose-5-phosphoric acid (Ba

salt, $[\alpha]_{\text{D}}^{25} -18.8^\circ$ in 0.1N-HCl; *di-brucine* salt, $[\alpha]_{\text{D}}^{25} -48.6^\circ$ in 50% aq. $\text{C}_5\text{H}_5\text{N}$). J. D. R.

Action of selenium sulphur protochloride and sulphur selenium protochloride on ethyl mercaptan and on ethyl selenomercaptan. A. BARONI (Atti R. Accad. Lincei, 1937, [vi], 26, 456–459).— $\text{S}:\text{Se}:\text{Cl}_2$ (A., 1938, I, 42) with EtSH or EtSeH in CS_2 gives the compounds $(\text{EtS})_2\text{Se}:\text{S}$, b.p. 102°, and $(\text{EtSe})_2\text{Se}:\text{S}$, b.p. 105°; similarly $\text{Se}:\text{S}:\text{Cl}_2$ (A., 1933, 241) gives the compounds $(\text{EtS})_2\text{S}:\text{Se}$, b.p. 104°, and $(\text{EtSe})_2\text{S}:\text{Se}$, b.p. 107°. With $\text{Pb}(\text{OH})_2\text{-NaOH}$, these yield PbS or PbSe, with $(\text{EtS})_2\text{Se}$ etc. E. W. W.

Selenoglycerols. A. BARONI (Atti R. Accad. Lincei, 1937, 26, 460–463; cf. A., 1936, 704).— NaSeH , from NaOEt and H_2Se , in EtOH, with $\text{OH}:\text{CH}_2:\text{CH}(\text{OH}):\text{CH}_2\text{Br}$ gives selenoglycerol, $\text{OH}:\text{CH}_2:\text{CH}(\text{OH}):\text{CH}_2\text{SeH}$, b.p. 185°/20 mm. Similarly with $\text{OH}:\text{CH}(\text{CH}_2\text{Br})_2$ and $\text{CHBr}(\text{CH}_2\text{Br})_2$, *di*-, *OH-CH}(\text{CH}_2\text{SeH})_2, b.p. 114°/20 mm., and *tri-selenoglycerol*, $\text{SeH}:\text{CH}(\text{CH}_2\text{SeH})_2$, b.p. 140°/20 mm, are obtained; the last is insol. in H_2O . E. W. W.*

Pyrolysis of esters in presence of aluminium chloride. H. GAULT and E. BELOFF (Bull. Soc. chim., 1938, [v], 5, 295–304).—When distilled with AlCl_3 , Bu^nOAc gives Bu^nCl , with HCl, CO_2 , CO, CH_4 , C_4H_8 , etc.; the reaction is primarily that of chlorolysis, not of catalytic decomp. Cetyl palmitate reacts similarly with AlCl_3 , but the non-volatile products are decomposed on heating, giving a mixture of ethylenic hydrocarbons. E. W. W.

Preparation of diacyloxy-derivatives of ketones, and a new method of preparation of acid anhydrides. V. V. EVLAMPIEV [with N. P. GURIANOV] (J. Gen. Chem. Russ., 1937, 7, 2934–2940).— Ac_2O and $\text{CMeR}(\text{OEt})_2$ ($\text{R} = \text{Me}$ or Et), at room temp. or at the b.p., yield EtOAc and AcOH , but not the expected $\text{CMeR}(\text{OAc})_2$. CPh_2Cl_2 and $\text{R}:\text{CO}_2\text{M}$ ($\text{R} = \text{Me}$, Pr , Ph , $\text{C}_{11}\text{H}_{23}$; $\text{M} = \text{Na}$, Ag) or $(\text{CH}_2:\text{CO}_2\text{Na})_2$ react at 100–130° as follows: $\text{CPh}_2\text{Cl}_2 + 2\text{R}:\text{CO}_2\text{M} \rightarrow (\text{R}:\text{CO}_2)_2\text{CPh}_2 \rightarrow \text{COPh}_2 + (\text{R}:\text{CO})_2\text{O}$. R. T.

Preparation of acetic anhydride by interaction of nitrogen peroxide and sodium acetate. V. M. RODIONOV and T. A. OBLITZEVA (Trans. VI Mendeleeev Congr. Chem. 1932, 1935, 2, Pt. 1, 1002–1003).—The reaction is $2\text{NaOAc} + 2\text{N}_2\text{O}_4 = \text{Ac}_2\text{O} + 2\text{NaNO}_3 + \text{N}_2\text{O}_3$. N_2O_3 does not act on NaOAc .

CH. ABS. (c)

Allylic transposition. VII. γ -Chloro- Δ^2 -propenyl acetate. A. KIRRMANN (Bull. Soc. chim., 1938, [v], 5, 256–260).— $\text{CH}_2\text{Cl}:\text{CH}_2:\text{CHCl}:\text{OAc}$ (I) and AgOAc-AcOH give $\text{CH}_2\text{Cl}:\text{CH}_2:\text{CH}(\text{OAc})_2$ (cf. A., 1936, 191), which can be distilled, b.p. 110–112°/11 mm., and is thus not an intermediate in the formation of $\text{CH}_2\text{Cl}:\text{CH}:\text{CH}:\text{OAc}$ (II) from $\text{CH}_2:\text{CH}:\text{CH}(\text{OAc})_2$ (III) and HCl (A., 1937, II, 175); similarly (I) is too stable to be an intermediate. The actual intermediate, α -chloro- Δ^2 -propenyl acetate (IV), b.p. 37°/12 mm., prepared from AcCl and $\text{CH}_2:\text{CH}:\text{CHO}$, spontaneously isomerises into (II), accompanied by some (I). With HCl at 0°, (IV) gives (I) and (II); with HBr, followed by HNO_3 , (IV) gives $\text{CH}_2\text{Br}:\text{CH}_2:\text{CO}_2\text{H}$. The presence of (IV) in the reaction product from (III)

is shown by the b.p. and Raman spectrum of the fraction of b.p. 30–40°/12 mm. E. W. W.

Vapour-phase photolysis of propionic acid.—See A., 1938, I, 318.

β -Methyl- α -propylvaleric acid and $\alpha\beta$ -dimethylhexoic acid. M. S. KONDAKOVA and M. M. KATZ-NELSON (Compt. rend. Acad. Sci. U.R.S.S., 1938, 18, 271–274).—*Propyl-sec.-butylmalonic acid*, m.p. 134–136° [from *sec.-Bu* bromide and $\text{CHPr}^{\alpha}(\text{CO}_2\text{Et})_2$], when heated yields β -methyl- α -propylvaleric acid, b.p. 233–234° (*Me* ester, b.p. 183–184°; *chloride*, b.p. 97–100°/37 mm.; *amide*, m.p. 125°; *anilide*, m.p. 110–111°). $\alpha\beta$ -Dimethylpentane- $\alpha\alpha$ -dicarboxylic acid, m.p. 139–140° [from *MeI* and $\text{CHMePr}^{\alpha}\text{CH}(\text{CO}_2\text{Et})_2$] (*Ag* salt), gives $\alpha\beta$ -dimethylhexoic acid, b.p. 223–224° (*Ag* salt; *Me* ester, b.p. 175–176°; *chloride*, b.p. 80°/25 mm.; *amide*, m.p. 121°). A. Li.

Addition of hydrogen bromide to undecenoic acid in toluene. I. Effect of reduced nickel. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1938, 13, 331–335; cf. A., 1937, II, 43; 1938, II, 48).—Addition of *HBr* to undecenoic acid in *PhMe* in presence of H_2 or in a vac. gives *l*-bromodecic acid with about 1% of the *κ*-bromo-acid (I), irrespective of dilution. In presence of either air or reduced Ni the proportion of (I) is greatly increased. The effect with air is > with Ni, and in both cases increases with dilution. F. L. U.

Unsaturated acids of natural oils. VII. Docosahexaenoic acid, abundant highly unsaturated acid of cod-liver oil. E. H. FARMER and F. A. VAN DEN HEUVEL (J.C.S., 1938, 427–430).—The C_{22} fraction isolated as *Me* ester from the unsaturated acids of cod-liver oil by evaporative distillation below 110° is a structurally homogeneous acid, $\text{C}_{22}\text{H}_{32}\text{O}_2$. Its mol. refraction shows it to be unconjugated, whilst complete reduction yields pure behenic acid. Oxidation with KMnO_4 and with O_3 shows that it has four $\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot$ groups between the end-groups $\text{CHMe}\cdot$ and $\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$. A. Li.

Substitution of iodine in enols by means of iodine and hydrogen peroxide. Preparation of ethyl α -iodoacetoacetate, *s*-iodoacetylacetone, and α -iodotetronic acid. W. D. KÜMLER (J. Amer. Chem. Soc., 1938, 60, 855–856).—With *I* and H_2O_2 in aq. EtOH $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, tetronic acid, and $\text{CH}_2\text{Ac}\cdot\text{COMe}$ give $\text{CHIAc}\cdot\text{CO}_2\text{Et}$ (I), α -iodotetronic acid, decomp. 160°, m.p. 170–175° (decomp.), and *s*-iodoacetylacetone, respectively. The products are unstable, especially in H_2O or when heated, and oxidise *KI* quantitatively. Only 1 *I* could be introduced. (I) is stable in H_2O_2 . R. S. C.

Condensation of formaldehyde with ethyl acetate. I, II. H. GAULT and J. BURKHARD (Bull. Soc. chim., 1938, [v], 5, 385–409, 409–429).—*I*. CH_2O , $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, and aq. K_2CO_3 under most conditions give known products, but condensation at –10° to 0° and removal of all H_2O at –15° yields *Et* $\alpha\alpha$ -di(hydroxymethyl)acetoacetate, an oil, which is stable when kept at room temp., but decomposes when heated to yield CH_2O . This product gives a *diacetate*, b.p. 172°/14 mm., and a *ketimine*, m.p. 185°, but with PhNCO gives only $\text{CO}(\text{NHPh})_2$ and with $\text{NHPh}\cdot\text{NH}_2$

gives $\text{CH}_2\text{N}\cdot\text{NHPh}$; with N_2H_4 it yields (?) $\alpha\alpha$ -di(hydroxymethyl)acetoacetylhydrazidephenylhydrazone (I), m.p. >300°; in boiling H_2O it liberates CH_2O and (?) $\text{CH}_2\cdot\text{CAc}\cdot\text{CO}_2\text{Et}$, and a similar decomp., followed by hydrolysis, is effected by hot, dil. H_2SO_4 ; *KOH* probably gives $\text{CHAc}(\text{CH}_2\cdot\text{OH})_2$. Unsuccessful attempts to prepare $\text{OH}\cdot\text{CH}_2\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ are described.

II. According to the temp. 1 mol. each of (I) and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ or CH_2O and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ with aq. K_2CO_3 give α -, m.p. 87° [*Ac* derivative (II), m.p. 79°; gives only oils with *CO*-reagents], and β -ethers, $\text{C}_{14}\text{H}_{22}\text{O}_7$, an oil, decomp. at the b.p./20 mm., which are possibly stereoisomeric forms of *Et*, 3-methyl-6-hydroxymethyl- Δ^3 -cyclohexenone-4 : 6-dicarboxylate. With NH_3 or $\text{NHPh}\cdot\text{NH}_2$ the β -ether gives derivatives of $\text{CH}_2(\text{CHAc}\cdot\text{CO}_2\text{Et})_2$ (III). CH_2O and (III) or 2 mols. of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and 3 mols. of CH_2O with aq. K_2CO_3 give a γ -ether, $\text{C}_{15}\text{H}_{24}\text{O}_8$, m.p. 101°, which with *CO*-reagents gives derivatives of (III), with $\text{AcCl}\cdot\text{C}_5\text{H}_5\text{N}$ gives (II), and may be *Et*, 3-hydroxy-3-methyl-4 : 6-di(hydroxymethyl)cyclohexanone-4 : 6-dicarboxylate. The ethers may have derived dicyclic structures since none of them gives a colour with FeCl_3 or shows *CO* bands in the Raman spectra. R. S. C.

Dissociation relationships of disubstituted succinic acids. H. BODE and K. PETERSEN (Ber., 1938, 71, [B], 871–879).—Re-examination of the dissociation const. of a series of symmetrical, disubstituted succinic acids shows that the relationship of Kuhn *et al.* (A., 1928, 507) does not exist. Examination of the models suggests that the quotient of the dissociation const. of symmetrically disubstituted succinic acids is smaller with the *meso*- than with the racemic form or the same for each. This is true for the halogeno- or alkyl-acids. If ring formation or internal subsidiary valency union prevents or greatly hampers free rotation the relationships may be displaced as shown experimentally and by model with cyclohexane derivatives and assumed to explain the abnormal relationships of the tartaric acids.

H. W.

Interaction of maleic acid with thiol compounds. E. J. MORGAN and E. FRIEDMANN (Biochem. J., 1938, 32, 733–742).—Maleic acid (I) forms an additive compound, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 140.5°, with $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (II), and similar compounds with cysteine (III), m.p. 134–135°, and with glutathione (IV), 151–152° (decomp.). In the course of reaction of (I) with (II) and (IV) fumaric acid (V) is formed. With increasing reaction concn. formation of the additive compound is more complete and less (V) is formed. Interaction of (I) with (III) is complete and no (V) is formed. A. T.

Synthesis of polyene fatty acids. J. BALTES (Fette u. Seifen, 1938, 45, 196–198).—A lecture. The synthesis of long-chain polyethylenic (fatty) acids is discussed with special reference to the work of R. Kuhn and collaborators. E. L.

Quantitative precipitation of citric acid. A. C. KUYPER (J. Biol. Chem., 1938, 123, 405–407).—When a citrate solution containing Ca^{++} and PO_4^{+++} is made alkaline, quant. pptn. of citrate occurs if the Ca^{++} present are in excess of those required to react

with PO_4''' and citrate. The ppt. is thought to be a complex of Ca'' , PO_4''' , and citrate. C. R. H.

Dissociation constants of some enols related to ascorbic acid. Tetronic, α -chloro-, -bromo-, -iodo-, and -hydroxy-tetronic acids, and ethyl α -iodoacetoacetate. W. D. KUMLER (J. Amer. Chem. Soc., 1938, 60, 859—864).—The following vals. of pK_a are determined: α -chloro- 2.13, α -bromo- 2.23, α -iodo- 2.31, and α -hydroxy-tetronic (I) 4.37, and tetronic acid (II) 3.76; $\text{CHIAc}\cdot\text{CO}_2\text{Et}$ 7.0. The strong acidities relative to ascorbic acid and $[\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}]_2$ are not due to fission of the lactone ring, since there is no second dissociation const., Na α -iodotetronate contains no extra H_2O , and *p*-nitrobenzyl α -bromotetronate, m.p. 177°, is not acidic. The results are ascribed to resonance between $\text{CH}_2\text{C}(\text{O}^-)\text{C}(\text{OH})\text{CO}$ and $\text{CH}_2\text{C}(\text{CO}\cdot\text{C}(\text{OH}))\text{C}\text{O}^-$, which also accounts for C_{13} , carrying the acidic OH and for (I) being weaker than (II). R. S. C.

Behaviour of halogen-substituted enols. Preparation of α -chlorotetronic acid. W. D. KUMLER (J. Amer. Chem. Soc., 1938, 60, 857—859).— α -Iodotetronic acid (I), $\text{CHIAc}\cdot\text{CO}_2\text{Et}$, and $\text{CHIAc}\cdot\text{COMe}$ react quantitatively with KI in strong acid solution, the reaction depending on one of the changes, $\text{C}(\text{OH})\cdot\text{Cl}\cdot\text{CO} + \text{H}^+ \rightarrow \text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO} + \text{I}^+$ or $\text{C}(\text{OH})\cdot\text{Cl}\cdot\text{CO} + \text{H}_2\text{O} \rightarrow \text{C}(\text{OH})\cdot\text{Cl}\cdot\text{CO} + \text{HOI}$. $\text{CHIAc}\cdot\text{CO}_2\text{Et}$ and (I) oxidise Fe^{II} to Fe^{III} , but α -bromotetronic acid (II) does so only in presence of KI (by replacement of the Br by I). By Kurt Meyer's method $\text{CHIAc}\cdot\text{CO}_2\text{Et}$ contains 20% of enol, or after 72 hr. in abs. EtOH 49%. Tetronic acid absorbs 20—35% more Br than corresponds with 100% of enol and α -Br- and α -I-derivatives apparently contain 20—35 and 50—70%, respectively, of enol. With HCl-abs. EtOH (II) gives α -chlorotetronic acid, m.p. 205° (decomp.), which slowly liberates I from KI (3% after 5 min.; 55% after 1 week), doubtless by replacement of Cl by I. The tenacity of the C-Hal linking is determined by the avidity of the halogen for its electron pair and thus on the size of the halogen atom; this determines the relative reactivities of the compounds. R. S. C.

Cacothelin as a reagent for ascorbic acid.—See A., 1938, III, 506.

Physico-chemical properties of ascorbic acid. J. C. GHOSH (J. Indian Chem. Soc., 1938, 15, 1—14).—Thiol and other compounds inhibit the auto-oxidation of synthetic acid. Potentiometric examinations of the alkali titrations of ascorbic (I) and dehydroascorbic acids and of the reversible (I) oxidation-reduction system are discussed in relation to mol. structures. The circular dichroism of (I) is investigated.

M. R.

Titrimetric determination of thionyl compounds. E. LARSSON (Svensk Kem. Tidskr., 1937, 49, 264—271).—The equilibrium in the reaction: $\text{S}[(\text{CH}_2)_n\cdot\text{CO}_2\text{H}]_2 + \text{Br} + \text{H}_2\text{O} \rightleftharpoons \text{OS}[(\text{CH}_2)_n\cdot\text{CO}_2\text{H}]_2 + \text{HBr}$ lies far to the left in AcOH containing $>0.2\%$ of H_2O , and may be used for the determination of thionyl acids by addition of KI and titration with

$\text{Na}_2\text{S}_2\text{O}_3$. The kinetics of the reaction have been studied. Benzylthionylacetic, m.p. 124°, β -thionylthiopropanoic, m.p. 114°, and *r*- β -thionylthiobutyric, m.p. 112°, acids have been prepared. M. H. M. A.

Thioketonic esters. V. S. K. MITRA (J. Indian Chem. Soc., 1938, 15, 31—36; cf. A., 1934, 57).— $\text{CHAc}(\text{CO}_2\text{Et})_2$ and $\text{H}_2\text{S}\cdot\text{EtOH}$ give *Et*₂ thioacetylmalonate, b.p. 120°/4 mm., converted by $\text{NHPh}\cdot\text{NH}_2$ into *Et* 1-phenyl-3-methyl-5-pyrazolone-4-carboxylate. $\text{CHMeAc}\cdot\text{CO}_2\text{Et}$ and $\text{H}_2\text{S}\cdot\text{EtOH}$ give *Et* methylthioacetoacetate (I), b.p. 95°/10 mm. *Et* isobutylthioacetoacetate, b.p. 122°/5 mm., is similarly prepared. As expected, $\text{SNa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ does not react with $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, but with $(\text{C}\cdot\text{CO}_2\text{Et})_2$ or $\text{CMeCl}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ gives *di*- β -carbethoxyisopropyl sulphide, b.p. 155°/12 mm., converted by $\text{NHPh}\cdot\text{NH}_2$ into 4-1'-phenyl-3'-methyl-4' : 5'-dihydropyrazolidene-1-phenyl-3-methyl-5-pyrazolone; this proves the attachment of the Na to S. The Na salt of (I) with Me_2SO_4 in hot EtOH gives the *S-Me*, b.p. 225°/750 mm. (from which HCl liberates MeSH), with EtI in C_6H_6 gives the *S-Et*, b.p. 220°/7 mm., and with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ in C_6H_6 the *S-CH}_2\cdot\text{CO}_2\text{Et}*-derivative, b.p. 160°/6 mm. With $\text{H}_2\text{S}\cdot\text{HCl}\cdot\text{EtOH}$ (I) gives *di*- γ -carbethoxy- Δ^{β} - β -butenyl disulphide, b.p. 180°/6 mm., also obtained by direct oxidation. The Na derivative of *Et*₂ thioacetonedicarboxylate (II) with Me_2SO_4 gives *Et*₂ β -methylthiolglutaconate, b.p. 135°/6 mm., and with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ the *S-CH}_2\cdot\text{CO}_2\text{Et}*-derivative, b.p. 170°/6 mm. With Ae_2O (II) gives the *S-Ac* derivative, b.p. 150°/9 mm., but with MgBu^+I merely liberates C_4H_{10} . R. S. C.

Formaldehyde from percarbonate.—See A., 1938, I, 319.

Reactivity of formaldehyde in presence of various bases.—See A., 1938, I, 316.

Aldol condensation products. M. M. PLANT (J.C.S., 1938, 536—541).—The action of CaO on crude aldol yields H_2O -sol. products, with reducing properties which appear to be due neither to unsaturation nor to CHO groups. Methylation followed by acetylation and fractionation yields acetates, $\text{C}_9\text{H}_{16}\text{O}_4$, b.p. 107°/21 mm., and $\text{C}_{13}\text{H}_{22}\text{O}_6$, b.p. 83°/0.15 mm. Structural formulae are suggested.

A. LI.

Enolisation and aldol condensation. K. F. BONHOEFFER and W. D. WALTERS (Z. physikal. Chem., 1938, 181, 441—448).—The aldol from MeCHO in presence of D_2O contains only a trace of D. The $(\text{CH}_2\cdot\text{CHO})^-$ ion formed in the enolisation of MeCHO reacts with MeCHO to form aldol before it can revert to MeCHO. This enolisation is the rate-determining step in Bell's measurements (A., 1937, I, 622). Similarly the product of the condensation of glyceraldehyde (I) alone, or of its mixture with dihydroxyacetone (II), to give ketohexoses contains only a trace of D if the reaction is carried out in D_2O . The ion $(\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{OH})^-$ reacts further before it can re-form (I) or (II). In the aldol condensation of COMe₂ on the other hand, the keto-enol equilibrium is established more rapidly than is the condensation equilibrium. H. J. E.

Treatment of the keto-enol equilibrium according to the theories of prototropy and mesomerism. C. GUSTAFSSON (Finska. Kem. Medd., 1938, 67, 12—18).—A theoretical discussion of the keto-enol equilibrium. M. H. M. A.

Interaction of ketones, carbon monoxide, and steam. D. V. N. HARDY (J.C.S., 1938, 464—468).—With CO and steam at 200 atm. pressure in presence of H_3PO_4 , COMe_2 (or $\text{CMe}_2\cdot\text{CH}\cdot\text{COMe}$) yields AcOH , $\text{Bu}^i\text{CO}_2\text{H}$ (ratio 2:1), and hydrocarbons, whilst COMeEt yields AcOH , EtCO_2H , $\text{CMe}_2\text{Et}\cdot\text{CO}_2\text{H}$, $\text{CMe}_2\text{Pr}\cdot\text{CO}_2\text{H}$, $\text{CMeEt}_2\cdot\text{CO}_2\text{H}$, and a neutral oil. With N_2 or H_2 instead of CO, COMe_2 gives AcOH with an increased yield of neutral oil, hydrogenation of which gives a fraction (b.p. $<200^\circ$) having an octane no. of 81. The mechanism of the reaction is discussed.

A. LI.

α -Chloroketones. G. RICHARD (Bull. Soc. chim., 1938, [v], 5, 286—294).—Theoretical. The greater reactivity of Cl in $\text{CHRCI}\cdot\text{CO}\cdot\text{CH}_2\text{R}'$ (I) than in $\text{COR}\cdot\text{CHCl}\cdot\text{CH}_2\text{R}'$ (II) is ascribed to enolisation of the former; various reactions are discussed, including the action of KCN. In the formation of $\text{CPh}_2\text{O} \rightarrow \text{CMe}\cdot\text{CN}$ from $\text{CPh}_2\text{Cl}\cdot\text{COMe}$, an intermediate *cyanohydrin*, $\text{CPh}_2\text{Cl}\cdot\text{CMe}(\text{OH})\cdot\text{CN}$, m.p. 197° , is isolated. With gaseous HCl, compounds of type $\text{CHR} \rightarrow \text{C}(\text{CN})\cdot\text{CH}_2\text{R}'$ and $\text{CN}\cdot\text{CR} \rightarrow \text{CH}\cdot\text{CH}_2\text{R}'$ regenerate the chloroketones (I) and (II). With $\text{EtOH}\cdot\text{HCl}$, (I) can give compounds of type $\text{CHRCI}\cdot\text{C}(\text{OH})(\text{CO}_2\text{Et})\cdot\text{CH}_2\text{R}'$. Some chloroketones with NaOPh give compounds of type $\text{COR}\cdot\text{CH}(\text{OPh})\cdot\text{CH}_2\text{R}'$, some of which when heated give *cyclobutadiones*. E. W. W.

Influence of radicals on isomeric transformations of *tert.* α -keto-alcohols. I. A. M. CHALETZKI (J. Gen. Chem. Russ., 1938, 8, 164—174).— γ -Keto- $\beta\beta\delta$ -trimethylhexane in H_2O and Br at 60° yield δ -bromo- γ -keto- $\beta\beta\delta$ -trimethylhexane (I), b.p. 82 — $83^\circ/10$ mm., which at 100° with 10% K_2CO_3 gives γ -hydroxy- $\beta\beta\delta$ -trimethylhexane $\gamma\delta$ -oxide (II), b.p. 62 — $63^\circ/10$ mm. (I) and KOAc in EtOH (6 hr. at the b.p.) yield γ -keto- δ -acetoxy- $\beta\beta\delta$ -trimethylhexane, b.p. 72 — $74^\circ/12$ mm., hydrolysed to (II) by 10% aq. K_2CO_3 . (II) when heated for 8 hr. with EtOH and H_2SO_4 at 120° yields β -keto- γ -hydroxy- $\delta\delta$ -dimethyl- γ -ethylpentane, b.p. 61 — $62^\circ/10$ mm. (semicarbazone, m.p. 198 — 199°), which is oxidised by K_2CrO_4 to AcOH and COEtBu^i , and is reduced by Na in EtOH to γ -hydroxy- $\beta\beta\delta$ -trimethylhexane, b.p. 168 — 170° (phenylurethane, m.p. 78 — 79°). R. T.

Amino-acid catalysis of the mutarotation of glucose. F. H. WESTHEIMER (J. Org. Chem., 1938, 2, 431—441).—17 NH_2 -acids, containing primary, *sec.*, *tert.*, or quaternary N, catalyse the mutarotation of glucose, their effects being approx. in accord with the Brønsted equation. Picoline and quinoline accord less well. R. S. C.

Dimethyl acetal of *d*-glucose. M. L. WOLFRAM and S. W. WAISBROT (J. Amer. Chem. Soc., 1937, 60, 854—855).—Glucose Et_2 mercaptal penta-acetate, CdCO_3 , and HgCl_2 in hot MeOH give *d*-glucose Me_2

acetal penta-acetate, m.p. 71 — 72° , $[\alpha]_D^{20} +12^\circ$ in CHCl_3 , converted by 0.4N-NaOMe at 0° into *d*-glucose Me_2 acetal, m.p. 94 — 95° , $[\alpha]_D^{20} +15^\circ$ in H_2O . R. S. C.

4:6-Dimethylaltrose and 2:4:6-trimethylaltrose from glucose. G. J. ROBERTSON and H. G. DUNLOP (J.C.S., 1938, 472—476).—4:6-Benzylidene-2:3-anhydro- α -methylalloside (I) (Robertson and Griffith, A., 1935, 1225) is hydrolysed by very dil. HCl in COMe_2 to a mixture of two α -methylhexoside chlorohydrins, m.p. 160 — 162° and 136 — 138° , $[\alpha]_D^{15} +113.1^\circ$ and $+157.2^\circ$ in MeOH, respectively. The mixture yields a triacetate with Ac_2O in $\text{C}_5\text{H}_5\text{N}$, and with Ag_2O gives 2:3-anhydro- α -methylalloside, m.p. 105 — 107° , $[\alpha]_D^{15} +153^\circ$ in MeOH, also obtained by hydrolysing (I) with $\text{H}_2\text{C}_2\text{O}_4$ in aq. COMe_2 . Methylation of this ($\text{MeI} + \text{Ag}_2\text{O}$) gives 4:6-dimethyl-2:3-anhydro- α -methylalloside, hydrolysed by KOH to 4:6-dimethyl- α -methylaltroside (identified by complete methylation), b.p. 130 — $135^\circ/0.5$ mm., $[\alpha]_D^{15} +145.7^\circ$ in CHCl_3 . Further hydrolysis (dil. HCl) affords 4:6-dimethylaltrose, m.p. 158 — 160° , $[\alpha]_D^{15} +102.9^\circ$ in H_2O (osazone, m.p. 139 — 141°). NaOMe converts the Me_2 anhydroalloside into 2:4:6-trimethyl- α -methylaltroside, b.p. $105^\circ/9.1$ mm., $[\alpha]_D^{15} +144.9^\circ$ in CHCl_3 , hydrolysed (dil. HCl) to 2:4:6-trimethylaltrose (a syrup), $[\alpha]_D^{15} +79.3^\circ$ in CHCl_3 , which yields the same osazone as 4:6-dimethylaltrose. A. LI.

Esters of methanesulphonic acid in the sugar group. B. HELFERICH and A. GNÜCHTEL (Ber., 1938, 71, [B], 712—718).— MeSO_2 , like *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$, derivatives of sugars crystallise readily and are well suited to identifications. Since the reactivity of MeSO_2Cl is $>$ that of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, the former gives many more derivatives than the latter and also reacts more readily. MeSO_3Na is converted by PCl_5 into MeSO_2Cl , from which the difficult removal of the last traces of P compounds is unnecessary. All esters of MeSO_2H give the Beilstein test for halogens by reason of the volatility of $(\text{MeSO}_2)_2\text{Cu}$ in the Bunsen flame. Esterification of individual OH-groups in presence of Ac or other groups is demonstrated by the production of β -*d*-glucose 1:2:3:4-tetra-acetate 6-methanesulphonate (mesylate) (I), m.p. 156° , $[\alpha]_D^{18} +10.3^\circ$ in CHCl_3 (whence bromoglucose triacetate 6-methanesulphonate, m.p. 91 — 93° , $[\alpha]_D^{18} +189^\circ$); glucose 1:2:3:6-tetra-acetate 4-methanesulphonate (II), m.p. 175 — 176° , $[\alpha]_D^{18} -20.1^\circ$ in CHCl_3 , 3:5-benzylidene-1:2-isopropylideneglucosulphonate 6-methanesulphonate, m.p. 132 — 133° , $[\alpha]_D^{18} +12.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and α -methyl-*d*-glucoside 2:3:4-triacetate 6-methanesulphonate, m.p. 113 — 114° , $[\alpha]_D^{20} +139^\circ$ in $\text{C}_5\text{H}_5\text{N}$, from the requisite OH-compound and MeSO_2Cl in $\text{C}_5\text{H}_5\text{N}$. The possibility of the introduction of several MeSO_2 groups is established by the prep. of 1:2-isopropylideneglucosulphonate 3:5:6-trimethanesulphonate, m.p. 165° , $[\alpha]_D^{20} -24.2^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and of α -*d*-methylglucoside 2:3:4:6-tetramethanesulphonate (III), m.p. 145 — 146° , $[\alpha]_D^{19} +92.2^\circ$ in CHCl_3 , in almost quant. yield. In this respect MeSO_2Cl is superior to *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$. Acetobromoglucose and MeSO_3Ag in C_6H_6 afford glucose 2:3:4:6-tetra-acetate 1-methanesulphonate, m.p. 112 — 113° , $[\alpha]_D^{19} +121.4^\circ$ in CHCl_3 , which reduces warm Fehling's solution, decomposes slowly when kept in a desiccator, and is transformed by CaCO_3 and

boiling MeOH into β -methylglucoside tetra-acetate. α -Glucose, MeSO_3Cl , and $\text{C}_5\text{H}_5\text{N}$ smoothly give 1-chloroglucose 2:3:4:6-tetramethanesulphonate, m.p. 168—169°, $[\alpha]_D^{20} + 110^\circ$ in EtOAc. KOAc and (III) in boiling Ac_2O give almost quantitatively α -methylglucoside 6-acetate 2:3:4-trimethanesulphonate, m.p. 146—147° (corr.), $[\alpha]_D^{20} + 90.6^\circ$ in $\text{C}_5\text{H}_5\text{N}$. With NaI in boiling COMe_2 or KI in boiling H_2O (III) yields α -methylglucoside 6-iodohydrin 2:3:4-trimethanesulphonate, m.p. 144—145°, $[\alpha]_D^{20} + 82.4^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Similarly (I) and NaI in COMe_2 at room temp. slowly yield β -d-glucose 6-iodohydrin 1:2:3:4-tetra-acetate and (II) with NaI in COMe_2 at 135° gives glucose 4-iodohydrin 1:2:3:6-tetra-acetate, m.p. 199—200° (slight decomp.) after softening at 190°, $[\alpha]_D^{20} + 51.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Hydrolysis of the sugar methanesulphonates does not proceed smoothly with the customary reagents. The marked discoloration suggests the elimination of MeSO_3H with production of unsaturated compounds. H. W.

Application of periodate to the volumetric determination of ketoses (monosaccharides). II. F. RAPPAPORT and I. REIFER (Mikrochim. Acta, 1938, 2, 273—279; cf. A., 1937, II, 530).—The ketose is oxidised with aq. KIO_4 at 100°, and the excess of IO_4^- is titrated iodometrically after buffering with K_2HPO_4 to prevent deposition of I from the IO_3^- . For a ketose containing n C atoms, $n - 2$ mols. of KIO_4 are consumed per mol. of ketose, as against $n - 1$ mols. in the case of aldoses and alcohols. Oxidation of 1 mol. of alcohol or ketose yields 2 mols. of CH_2O and $n - 2$ mols. of HCO_2H , as compared with 1 mol. of CH_2O and $n - 1$ mols. of HCO_2H formed from 1 mol. of aldose. The method therefore affords distinction between the three classes of compounds. J. W. S.

Bromine oxidation and mutarotation measurements with α -d- β -mannoheptose and α -d- α -guloheptose. H. S. ISBELL (J. Res. Nat. Bur. Stand., 1938, 20, 97—108).—With $\text{NaCN} \cdot \text{CaCl}_2$ mannose gives much d- α - (Pb, $+\text{H}_2\text{O}$, and K, $[\alpha]_D^{20} + 5.4^\circ$ in H_2O , salts; best isolated as Ba or Ca salt) and some d- β -mannoheptonic acid [best isolated as Pb salt, $[\alpha]_D^{20} + 2.6^\circ$ in H_2O ; K salt, $[\alpha]_D^{20} + 0.3^\circ$ in H_2O ; γ -lactone, (I), m.p. 130°, $[\alpha]_D^{20} - 35.7^\circ \rightarrow$ (slowly) -27.9° in H_2O], epimerised in $\text{C}_5\text{H}_5\text{N}$. Na-Hg reduces (I) to α -d- β -mannoheptose (II), $+\text{H}_2\text{O}$, m.p. 83°, $[\alpha]_D^{20} + 45.7^\circ \rightarrow +14.5^\circ$ in H_2O (cf. Ettcl, A., 1933, 47). α -d- α -Mannoheptose, m.p. (anhyd.) 140° and $(+\text{H}_2\text{O})$ 107°, is described. Equilibration of crude d- α -mannoheptose in H_2O yields β -d- α -mannoheptose, $+\text{H}_2\text{O}$, m.p. 104°. Mutarotation of (II) involves a fast reaction to an unstable isomeride, followed by a slow reaction. The temp. coeff. for the fast reaction is similar to that for the fast reactions of similar sugars, e.g., talose, that for the slow reaction corresponding with the normal $\alpha \rightleftharpoons \beta$ change. Br-oxidation of (II) and α -d- α -guloheptose consists of fast, followed by slow, reactions (cf. talose), the amounts of readily oxidisable forms indicated being 38 and 33%, respectively. The peculiarities of mutarotation and oxidation are determined by the configuration of the C of the pyranose ring, thus showing the advantage of the author's system of classification. R. S. C.

G* (A., II.)

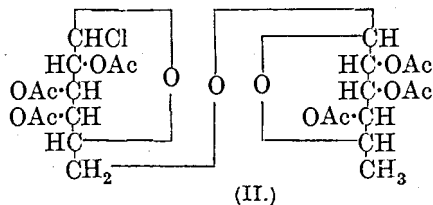
Acetylation of perseulose. Y. KHOUVINE and G. ARRAGON (Compt. rend., 1938, 206, 917—919; cf. A., 1909, i, 634).—Perseulose (I) and $\text{Ac}_2\text{O} \cdot \text{C}_5\text{H}_5\text{N}$ at room temp. for 24 hr. give a hexa-acetate (II), m.p. 105°, $[\alpha]_{578}^{20} + 0.57^\circ$ in CHCl_3 , $+20.8^\circ$ in C_6H_6 , -2.85° in MeOH, which shows a strong absorption band at 2800 μ , characteristic of C:O. (I) and $\text{Ac}_2\text{O} \cdot \text{ZnCl}_2$, at room temp. for 24 hr., give (II) and a hexa-acetate, m.p. 112°, $[\alpha]_{578}^{20} - 113.4^\circ$ in CHCl_3 , -113.2° in C_6H_6 , -106.5° in MeOH, which shows no characteristic absorption band and probably has a cyclic structure. An alcohol, m.p. 91°, $[\alpha]_{578}^{20} - 12^\circ$ in CHCl_3 , -7.42° in C_6H_6 (Alc_7 derivative), is recorded. A. T. P.

Influence of neutral salts on inversion of sucrose.—See A., 1938, 1, 316.

Inhibition in inversion of sucrose.—See A., 1938, 1, 316.

Synthesis of crystalline 6- β -d-glucosido- α -d-mannose, the epimeride of gentiobiose, and its octa-acetate. H. J. DAUBEN, jun., and W. L. EVANS (J. Amer. Chem. Soc., 1938, 60, 886—890).— β -Gentiobiose octa-acetate, m.p. 196°, $[\alpha]_D^{24} - 6.8^\circ$, yields 57% of acetobromogentiobiose and thence by Zn-75% AcOH at 0° 96% of gentiobial hexa-acetate, m.p. 121—122°, $[\alpha]_D^{18} - 7.4^\circ$ in CHCl_3 . With $\text{Ba}(\text{OMe})_2$ this gives 65% of gentiobial, m.p. 191—192°, oxidised by BzO_2H in 68% yield to 6- β -d-glucosido- α -d-mannose, m.p. $(+\text{H}_2\text{O})$ 137—138°, (anhyd.) 167.5—168°, $[\alpha]_D^{20} - 5.09^\circ \rightarrow -11.06^\circ$ in about 2 hr. in H_2O , which by acid hydrolysis gives glucose and mannose and with $\text{C}_5\text{H}_5\text{N} \cdot \text{Ac}_2\text{O}$ at 0° affords the octa-acetate, dimorphic, m.p. 114° and 142—143°, respectively, $[\alpha]_D^{21} + 26^\circ$ in CHCl_3 . M.p. are corr. $[\alpha]$ agree with Hudson's rules. R. S. C.

Action of mercury salts on acetohalogeno-sugars. XI. Synthesis of derivatives of β -1-l-rhamnosido-6-d-galactose. G. ZEMPLÉN, A. GERECs, and H. FLESCH (Ber., 1938, 71, [B], 774—776).—Galactosan triacetate is converted by TiCl_4 in CHCl_3 into 1-chlorogalactopyranose 2:3:4-triacetate (I), m.p. 132°, $[\alpha]_D^{21} + 207.8^\circ$ in CHCl_3 , transformed by acetobromorhamnose and $\text{Hg}(\text{OAc})_2$ in abs. C_6H_6 at 50° into α -1-chloro- β -6-l-rhamnosido-d-galactopyranose hexa-acetate (II), m.p. 166.5—167.5°, $[\alpha]_D^{21} + 67.59^\circ$ in



CHCl_3 , whence, by Ac_2O and AgOAc , a rhamnosido-galactose hepta-acetate, m.p. 84—85° after softening at 71°, $[\alpha]_D^{21} - 9.90^\circ$ in CHCl_3 . Successive treatments of (I) with $\text{Hg}(\text{OAc})_2$ in C_6H_6 at 50°, Ag_2CO_3 in boiling MeOH, and $\text{Ac}_2\text{O} \cdot \text{NaOAc}$ afford β -1-methyl- β -6-l-rhamnosido-d-galactopyranose hexa-acetate, m.p. 161.5—162.5°, $[\alpha]_D^{17} - 39.21^\circ$ in CHCl_3 , identical with a fraction obtained by crystallisation of β -1-methyl-robinobiose hexa-acetate. H. W.

Methylation of raffinose. K. HESS and K. H. LUNG (Ber., 1938, 71, [B], 827—829).—Anhyd.

raffinose is converted by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at room temp. into the hendeca-acetate, m.p. 99.8° , $[\alpha]_D^{20} +104.6^\circ$ in CHCl_3 . This is pre-methylated by Me_2SO_4 and 30% NaOH at 50° and the product is treated with Na in liquid NH_3 and then with MeI , thus giving hendeca-methylraffinose, b.p. $155\text{--}165^\circ/0.001\text{ mm.}$, $[\alpha]_D^{20} +124.1^\circ$ in H_2O , without appreciable amounts of more volatile fractions. It therefore appears that saccharide linkings are not sensitive to Na-NH_3 . H. W.

Decomposition products of sugars. Caramel and humin. A. SCHWEIZER (Rec. trav. chim., 1938, 57, 345—382).—The literature of caramel and humin is reviewed. Sugar-humin $[(\text{C}_{24}\text{H}_{10}\text{O}_9)_n \text{ or } (\text{C}_{12}\text{H}_5\text{O}_4)_n]$ (I) (Cl_4 - and Br_4 -derivatives) is a highly dehydrated carbohydrate, highly polymerised, with the hexane skeleton intact. A mechanism of formation from hyamatomelanin acid or isosaccharosan (II) is discussed. (I) and H_2O_2 - KOH yield CO_2 and a product, $\text{C}_{12}\text{H}_{10}\text{O}_5$ (III) (structure suggested) (cf. hyamatomelanin acid, Bergius, Naturwiss., 1928, 16, 4) [Pb and K salts; NHPh-NH_2 compound; Ac_2 derivative; Br_2 -derivative (Br in N_2 for 6 hr.)], which with HNO_3 (d 1.52) at -5° gives a substance (V), $\text{C}_{12}\text{H}_{11}\text{O}_8\text{N}$, decomp. explosively about 160° , $\text{H}_2\text{C}_2\text{O}_4$, and saccharomono-lactone. (V) [also obtained from (I)] and HNO_3 (d 1.4), or H_2O_2 - KOH , give saccharic and oxalic acids. (I) and HNO_3 (d 1.52) at below 60° afford $\text{H}_2\text{C}_2\text{O}_4$ and saccharodilactone, and HNO_3 (d 1.26) gives a gluconolactone, m.p. 143° (Ac_3 derivative, m.p. 115°). Caramel is a mixture of (I) and (II), as also are caramelan, caramelen, and caramelin. A. T. P.

Synthesis and properties of β -alkylglucosides.
II. Glucosides of five butyl alcohols and of tertiary amyl, hexyl, and heptyl alcohol. S. VEIBEL and H. LILLELUND (Bull. Soc. chim., 1938, [v], 5, 494—502; cf. A., 1936, 318).—Acetobromoglucose, $\text{Bu}^\text{t}\text{OH}$, and Ag_2CO_3 give β -*n*-butylglucoside tetra-acetate, m.p. $65.5\text{--}66.5^\circ$, $[\alpha]_D^{20} -26.8^\circ$ in EtOH , hydrolysed to β -*n*-butylglucoside, m.p. $68\text{--}69^\circ$, $[\alpha]_D^{20} -36.9^\circ$ in H_2O , not hygroscopic when pure. β -*tert*-Butyl-, m.p. $164\text{--}166^\circ$, $[\alpha]_D^{20} -19^\circ$ in H_2O (tetra-acetate, m.p. $145\text{--}146^\circ$, $[\alpha]_D^{20} -19.3^\circ$ in EtOH), -dimethylethylcarbiny-, m.p. $127\text{--}128^\circ$, $[\alpha]_D^{20} -18^\circ$ in H_2O (tetra-acetate, m.p. $122.5\text{--}123.5^\circ$, $[\alpha]_D^{20} -17.7^\circ$ in EtOH), -methyldiethylcarbiny- (tetra-acetate, m.p. $96\text{--}97^\circ$, $[\alpha]_D^{20} -14.5^\circ$ in EtOH), and -triethylcarbiny-glucoside, $+\text{H}_2\text{O}$ (tetra-acetate, m.p. $94\text{--}95^\circ$, $[\alpha]_D^{20} -10.3^\circ$ in EtOH), are similarly prepared. *dl*- $\text{CHMeEt}\cdot\text{OH}$ gives β -*l*-, m.p. $75\text{--}76^\circ$, $[\alpha]_D^{20} -44.5^\circ$ in H_2O (tetra-acetate, m.p. $127\text{--}128^\circ$, $[\alpha]_D^{20} -36.6^\circ$ in EtOH), and β -*d*-sec.-butylglucoside, m.p. $116\text{--}117^\circ$, $[\alpha]_D^{20} -32.1^\circ$ in H_2O (tetra-acetate, m.p. $101\text{--}103^\circ$, $[\alpha]_D^{20} -18.5^\circ$ in EtOH), the synthesis being slightly asymmetric; hydrolysis yields pure *l*- and *d*- $\text{CHMeEt}\cdot\text{OH}$ (*p*-nitrobenzoates, m.p. $17.5\text{--}18^\circ$, $[\alpha]_D^{20} 30.2^\circ$ in abs. EtOH). *dl*-sec.-*Bu* *p*-nitrobenzoate has m.p. $25\text{--}26^\circ$. R. S. C.

Enzymic hydrolysis of triethylcarbinol- β -*d*-glucoside. Steric hindrance: its significance in the hydrolysis of glucosides. S. VEIBEL and H. LILLELUND (Z. physiol. Chem., 1938, 253, 55—63; cf. A., 1936, 1235; 1937, III, 30).—In the hydrolysis, at 30° and 20° , by emulsin (I) of triethylcarbinol- β -*d*-glucoside (II) $k \times 10^4$ decreases from 2.98 and 0.905

at the start to 1.32 and 0.45, respectively, at 49 hr. The affinity of (I) for (II) is approx. 25 times that of (I) for trimethylcarbinol- β -*d*-glucoside (III) and (II) is hydrolysed by (I) approx. 4 times as rapidly as is (III). The concn. of (III) required to bind a given percentage of (I) is 25 times that of (II). Methyldiethylcarbinol- β -*d*-glucoside is hydrolysed by (I) approx. 15 times as rapidly as is (III). Steric hindrance is not a cause of the slow hydrolysis of the glucosides of *tert*. alcohols. W. McC.

Attempted separation of the isomorphous glucosides of *Digitalis lanata*. C. MANNICH and F. BORKOWSKY (Arch. Pharm., 1938, 276, 234—242).—The possibility of converting the glucosides into non-isomorphous derivatives which can be separated from one another by crystallisation and from which the parents can be readily regenerated has been examined. The crude glucoside (I) is readily dissolved by COMe_2 containing 0.3% of HCl (H_2SO_4 and CuSO_4 behave similarly) but dissolution is accompanied by rapid hydrolysis although the material is relatively stable towards 0.3% $\text{HCl-H}_2\text{O}$ or 0.3% HCl-EtOH . If, immediately after dissolution of (I) in 0.3% HCl-COMe_2 , the solution is diluted with H_2O , the products are a trisaccharide acetate hydrolysed to AcOH , digilanidobiose, and digitoxose (II) and a portion sol. in CHCl_3 which contains unchanged (I) and some genin but is mainly glucosidic since it gives (II) when hydrolysed. H. W.

Attempted syntheses of hydroxyflavanone-glucosides. S. FUJISE and S. MITUI (Ber., 1938, 71, [B], 912—915).—7-Hydroxyflavanone, acetobromoglucose, Ag_2O , and quinoline in C_6H_6 give 7-hydroxyflavanoneglucoside tetra-acetate, m.p. $149.5\text{--}150^\circ$, $[\alpha]_D^{25} -21.0^\circ$ in dioxan, hydrolysed by NaOH in MeOH-CHCl_3 to 7-hydroxyflavanone-7-glucoside ($+\text{H}_2\text{O}$), m.p. $183\text{--}184^\circ$, $[\alpha]_D^{25} -102.63^\circ$ in dioxan or (anhyd.), $[\alpha]_D^{25} -121.34^\circ$ in dioxan. Similarly 5:7-dihydroxyflavanone (I) gives 5:7-dihydroxyflavanone-7-glucoside tetra-acetate (II), m.p. $173\text{--}173.5^\circ$, $[\alpha]_D^{21} -29.1^\circ$ in dioxan, the constitution of which follows from its indifference towards CH_2N_2 , which readily converts (I) into 5-hydroxy-7-methoxyflavanone. Ac_2O and $\text{C}_5\text{H}_5\text{N}$ transform (II) into 7-hydroxy-5-acetoxyflavanone-7-glucoside tetra-acetate, m.p. $160.5\text{--}161^\circ$, reconverted into (II) by HBr-AcOH . 5:7-Dihydroxyflavanone-7-glucoside ($+\text{H}_2\text{O}$), has m.p. $134\text{--}135^\circ$ (decomp.), $[\alpha]_D^{25} -36.0^\circ$ in CHCl_3 . H. W.

Synthesis of quinacetophenone methyl ether glucoside. F. MAUTHNER (J. pr. Chem., 1938, [ii], 150, 197—198).—Addition of aq. NaOI to 3:6- $\text{OMe-C}_6\text{H}_3(\text{OH})\cdot\text{COMe}$ and acetobromoglucose in COMe_2 at 5° gives 2-aceto-4-methoxyphenylglucoside tetra-acetate, m.p. $159\text{--}160^\circ$, converted by 6% aq. $\text{Ba}(\text{OH})_2$ into the free glucoside, m.p. $139\text{--}140^\circ$ (cf. Goris and Canal, A., 1935, 1041). R. S. C.

Structure of dextran. F. E. BRAUNS (Canad. J. Res., 1938, 16, B, 73—75).—Re-examination of the data recorded by Fowler *et al.* (A., 1938, II, 55) for the dextran synthesised by the action of *Leuconostoc mesenteroides* on sucrose reveals the impossibility of thus deciding definitely whether it is a 1:2:1, 1:3:1, or 1:4:1 polymeride. H. W.

Pectic substances. I. The araban and pectic acid of the peanut. E. L. HIRST and J. K. N. JONES (J.C.S., 1938, 496—505).—The polysaccharides of *Arachis hypogaea* contain starch, cellulose, and a complex of pectic acid and araban. Partial methylation (Tl derivative with MeI) of the complex yields the methylated araban, hydrolysed by 1% MeOH-HCl to 3 products: (a) 2:3:5-trimethylmethyl-1-arabinoside, b.p. 87—90°/0.001 mm., $[\alpha]_D^{25}$ -60° in H₂O, hydrolysed by dil. HCl to the trimethylarabinose, oxidised (Br) to the γ -arabonolactone, converted by MeOH-NH₃ into the arabanamide; (b) 2:3-dimethylmethyl-1-arabinoside, b.p. 115—122°/0.001 mm., $[\alpha]_D^{25}$ +14° in H₂O, hydrolysed to 2:3-dimethyl-1-arabinose, $[\alpha]_D^{20}$ +106° in H₂O, oxidised to the γ -lactone, b.p. 145—155°/0.003 mm., $[\alpha]_D^{20}$ -34° in H₂O, giving an amide, m.p. 160°, $[\alpha]_D^{20}$ +17° in H₂O, which gives a negative Weerman test; and (c) 3-methylmethyl-1-arabinoside, b.p. up to 200°/0.001 mm., $[\alpha]_D^{25}$ +46° in H₂O, giving the 3-methylarabinose (impure), $[\alpha]_D^{20}$ +96° in H₂O, γ -lactone, b.p. 175°/0.003 mm., $[\alpha]_D^{25}$ -36° in H₂O, and amide, $[\alpha]_D^{25}$ +31° in H₂O, the hydrazodicarbonamide from which (Weerman) was identical with an authentic sample. The structure of the araban is discussed. A. LI.

Degradation of limit dextrins and starch by acetyl bromide. II. Constitution of limit dextrins and of starch. K. MYRBÄCK (Svensk Kem. Tidskr., 1937, 49, 271—274; cf. A., 1937, II, 446).—Zulkowski starch and maltose when treated with AcBr-AcOH and then with Ag₂CO₃ in Et₂O give maltose hepta-acetate (I) in good yield; under identical conditions (I) is not obtained from a limit dextrin of mol. wt. about 610. Similar observations are recorded with a sol. starch and a limit dextrin of mol. wt. about 810. A part of the starch mol. therefore is not formed from maltose residues and the limit dextrins arise from the portions of the mol. which are not constructed according to Haworth's formula.

H. W.

Degradation products of starch produced by α -amylase. J. BLOM, B. BRAAL, and A. BAK (Z. physiol. Chem., 1938, 252, 261—270).—Potato starch is hydrolysed by α -amylase yielding dextrins and maltose (I). The quantity of (I), which is determined by the difference in the reducing power of the sugars before and after fermentation with yeast, increases with degree of degradation and reaches a max. of 23% of the theoretical quantity when 40% of the starch is hydrolysed. The hydrolysis by α -amylase is inhibited by increasing quantities of (I).

J. D. R.

Periodic acid oxidation of starches and dextrins as a means of determining molecular size. C. G. CALDWELL and R. M. HIXON (J. Biol. Chem., 1938, 123, 595—606).—HIO₄ consumed in oxidation of starches and dextrin fractions varies inversely with the fat and P content. Hydrolysis of oxidised starch (0.004N-H₂SO₄) gives (CHO)₂, indicating cleavage of the non-terminal glucose units between C₍₂₎ and C₍₃₎. Correlation between the amount of CH₂O formed in oxidation and the reducing power of nine dextrins shows that both methods are reliable for the determination of reducing terminal groups, and it is

concluded that starches have chain-lengths > the 25 units proposed by Haworth. J. D. R.

Starch. IX. Constitution of starch on the basis of the determination of the terminal group. K. HESS and K. H. LUNG (Ber., 1938, 71, [B], 815—826; cf. A., 1937, II, 326).—Treatment of potato starch with Me₃SO₄ and 45% NaOH in H₂ gives methylstarch with 42—43% OMe which, when examined by the terminal group method of Hess and Neumann (*ibid.*, 232), shows an end-group content of 1.88—1.90%, indicating a degree of polymerisation of 52—52.4. The viscosity of trimethylstarch in CHCl₃ indicates a 30- to 60-fold greater degree of polymerisation. The discrepancy leads to the examination of the "comb formula" for starch by determination of the less highly methylated sugars formed by hydrolysis and also by measurements of viscosity; the comparison gives little support to the formula. Other possibilities for the constitution of starch are discussed. H. W.

Viscosimetric behaviour of solutions of methylstarch. W. PHILIPPOFF and K. HESS (Ber., 1938, 71, [B], 841—847).—The viscosities of the trimethylstarches of Hess and Lung (preceding abstract) have been determined in CHCl₃. The observed vals. are > any recorded previously and are very similar to those of the starch triacetate of Sakurada and Lee. This is attributed to the very mild conditions during extraction of the starch and prep. of the derivatives. Typical micellar solutions such as those of soap colloids and of methylstarch (I) in which according to Hess and Lung (*loc. cit.*) individual mols. cannot be present have mechanical properties exactly similar to those of cellulose derivatives and caoutchouc. Although the flow behaviour of solutions of (I) and methylcellulose is closely similar the latter gives normal films of high tenacity whereas the former usually gives only very brittle and powdery films. In harmony with results obtained with the ultracentrifuge, starch, in contrast with cellulose, appears highly heterodisperse.

H. W.

Action of nucleotides in disruptive phosphorylation of glycogen.—See A., 1938, II, 510.

Mechanism of cellulose reactions. H. M. SPURLIN (Trans. Electrochem. Soc., 1938, 73, Preprint 30, 411—423).—Cellulose reactions are classified as (a) formation of derivatives of OH groups and (b) degradation of the chain-mols. by hydrolysis, oxidation, or decomp. In a partly substituted product the distribution of substituents is governed by the laws of chance, modified to some extent by the tendency of particular groups to react more rapidly than the remainder in certain reactions (*e.g.*, etherification) and also by the degree of swelling of the cellulose, the rate of diffusion of the reagents, and the solubility of the product. When swelling is low the reaction proceeds in bands from visible starting points on the surface. In solution, or with rapid intramolecular swelling, the reaction is uniform throughout. When intermolecular swelling occurs, although the reaction is not visibly heterogeneous, the X-ray diagram of the original cellulose persists for a long time.

W. A. R.

Terminal group question of cellulose in cotton hairs. II. E. LECKZYCK (Ber., 1938, 74, [B], 829—841).—Re-examination of the "terminal group" method of Hess and Neumann (A., 1937, II, 232) with mixtures of tetra- (I) and tri-methylmethylglucoside shows that it is sufficiently sensitive for chain-lengths up to 10,000 C₆ and could be extended to longer chains by working at greater dilutions. The purification of the cotton hairs is effected under the conditions used by Hess and Neumann (*loc. cit.*) but with inclusion of a final treatment with 9% NaOH. The fibre thus obtained gives a "terminal group prep." in very small amount; this is very extensively decomposed by repeated distillation over Na and appears to consist mainly of the Me ester of a methoxycarboxylic acid. The more complete removal of the "accompanying matter" by the NaOH is accompanied therefore by the formation of decomp. products in small amount. The extracted material when treated with alkali and Me₂SO₄ gives a product with low OMe content which cannot be distilled unchanged over Na; it does not appear to be related to the carbohydrate group and probably arises from the fat-wax phase of the cotton hairs. A "terminal group prep." obtained from cotton exposed to air during preliminary purification and methylation is found to consist largely of a Me trimethoxybutan(?)onecarboxylate. A second prep. in which methylation at any rate was accomplished with exclusion of air gave, after hydrolysis, small amounts of tetramethylglucose, so that (I) in small amount can result from secondary decomp. The experimental results prove the necessity of excluding all formulae for cellulose which have a chain-length up to 10,000 C₆. The possibilities remain that the cellulose chain is so highly polymerised that the terminal group cannot be detected by the method of Hess and Neumann (degree of polymerisation >10⁴ C₆), that the terminal group is a glucose group with "anhydride closure" with respect to C₄, or that cellulose has not a chain but a ring structure. In the second case dimethylglucose must be formed by hydrolysis of the methylcellulose; this is not experimentally excluded but the required structure is regarded as unlikely.

H. W.

Reduction of aminosorbitol hydrochloride with hydriodic acid. P. A. LEVENE and C. C. CHRISTMAN (J. Biol. Chem., 1938, 123, 77—82; cf. A., 1937, II, 139; 447).—Reduction of aminosorbitol (I) hydrochloride by HI yields β -aminohehexene oxide (platinchloride; hydrochloride, m.p. 217—218°, $[\alpha]_D^{25}$ -5.9° in EtOH; Ac derivative, m.p. 142—143°, $[\alpha]_D^{25}$ +4.1° in EtOH) which cannot be hydrogenated. The hexa-acetate of (I) with HI in AcOH gives a β -aminohehexanol, m.p. 86—88° (Ac derivative, m.p. 77—78°, $[\alpha]_D^{25}$ +39.7° in CHCl₃).

E. G. B.

Effect of heating amino-acids in neutral or acid solution in the autoclave. N. I. GAVRILOV, N. V. ELAGUINA, N. V. DUDIKINA, and I. V. KORNILOV (Bull. Soc. chim., 1938, [v], 5, 442—454).—Arginine and (NH₂)₁-acids, except cystine, yield only traces of NH₃ in H₂O at 180°/10 atm. Glycine anhydride and alanyl-glycine yield slightly more NH₃ than do the component acids and glutamic acid

gives its lactam. These changes are reduced by increasing acidity. Histidine yields NH₃ with fission of the ring, the change being favoured by acid.

R. S. C.

Bacterial deamination of glycine. F. EGAMI (Bull. Soc. Chim. biol., 1938, 20, 301—304; cf. A., 1936, 113, 640).—An organism isolated from garden soil deaminates and dehydrogenates glycine with formation of CHO·CO₂H.

J. N. A.

Determination of arginine and histidine. G. MOUROT and O. HOFFER (Bull. Soc. Chim. biol., 1938, 20, 274—292).—Three methods for separation and determination of arginine (I) and histidine (II) are described: (a) (II) is pptd. by AgOAc in presence of Ba(OH)₂ whilst (I) remains in solution; (b) when (I) and (II) are heated with dil. alkali in sealed tubes, (I) is decomposed into NH₃ and ornithine, whilst (II) is unattacked; (c) arginase or the crude enzyme prep. from liver decomposes (I) into CO(NH₂)₂ and ornithine, without affecting (II). The three methods are applicable to protein hydrolysates; (a) and (b) can be applied only after a quant. separation of (I) and (II) from the other NH₂-acids, whilst (c) can be used directly. In the last case the errors are 1% for (I) and 2% for (II).

J. N. A.

Reduction of glucosamic acid with hydrogen iodide in glacial acetic acid. P. A. LEVENE and C. C. CHRISTMAN (J. Biol. Chem., 1938, 123, 83—85; cf. A., 1903, i, 74; 1935, 1228).—Reduction of glucosamine by HI in AcOH yields α -amino- γ -hydroxyhexoic acid, $[\alpha]_D^{25}$ -16.4° in 20% HCl.

E. G. B.

Oxazolines and thiazolines. IV. β -Chloroethylthiourethane. P. G. SERGEEV and B. S. KOLITSCHIEV (J. Gen. Chem. Russ., 1937, 7, 2863—2867).—CH₂Cl·CH₂·CNS (I) in Et₂O·EtOH and HCl at 0° yield β -chloroethylthiourethane (II), m.p. 106—107°, regenerating (I) when distilled from P₂O₅ in vac. and identical with the product obtained previously (A., 1938, II, 32) from OH·CH₂·CH₂·CNS and HCl at 80°. (II) is also synthesised from CH₂Cl·CH₂·S·COCl and NH₃.

R. T.

Thiocarbamyl ethers. M. BATTEGAY and R. KREBS (Compt. rend., 1938, 206, 919—921).—Anhyd. Pr^oOH and NH₄CNS at <10° and H₂SO₄·H₂O give the compound, OPr^o·CS·NH₂, m.p. 35°; if the reaction mixture is not neutralised and alcohol removed in presence of mineral acid, conversion (at about 80°) into the substance, SPR^o·CO·NH₂, m.p. 91°, occurs.

A. T. P.

Reduction of nitrous acid by cysteine and glutathione. M. LEMOIGNE, P. MONGUILLON, and R. DÉSVEAUX (Compt. rend., 1938, 206, 947—949).—At p_H 3 cysteine and glutathione rapidly reduce HNO₂ to NH₂OH and NH₃, whilst at p_H 7 <30% of the HNO₂ is reduced by glutathione.

P. G. M.

Synthesis of tetradeuterohomocystine and dideuteromethionine. W. I. PATTERSON and V. DU VIGNEAUD (J. Biol. Chem., 1938, 123, 327—334; cf. A., 1935, 1486).—C₂D₂, from CaC₂ and D₂O, is reduced (CrCl₂) to C₂H₂D₂, brominated to C₂H₂D₂Br₂ (yield from D₂O, 63%). The latter is condensed with CH₂Ph·SH to $\alpha\beta$ -dideutero- β -benzylthioethyl bromide, b.p. 118—123°/1 mm. (yield 41%), which with

$\text{CHNa}(\text{CO}_2\text{Et})_2$ yields 65% of $\beta\gamma$ -dideutero-*benzylthioethylmalonic acid*, m.p. 119–120°. By successive bromination and amination this yields 66% of $\beta\gamma$ -dideutero-*S-benzylhomocysteine*, indistinguishable from *S-benzylhomocysteine*. This compound by successive reduction and oxidation (cf. A., 1935, 737) yields 90% of $\beta\beta'\gamma\gamma'$ -tetra-deutero-homocystine, and by successive reduction (Na) and methylation (MeI) in liquid NH_3 , 78% of $\beta\gamma$ -dideutero-methionine. The last two compounds contain theoretical amounts of D, indicating stability of D in these positions.

E. G. B.

Guanidine structure and hypoglycæmia. Branched-chain analogue of synthalin. C. E. BRAUN and B. J. LUDWIG (J. Org. Chem., 1938, 2, 442–446).—Et γ -cyano- $\epsilon\eta$ -dimethyloctane- γ -carboxylate (prepared from $\text{CHMeBu}^\beta\text{CH}_2\text{Br}$ and $\text{CN}\cdot\text{CHET}\cdot\text{CO}_2\text{Et}$), b.p. 99–105°/3–4 mm., gave the corresponding cyano-amide, m.p. 74°, by way of the acid and acid chloride, but not directly by NH_3 etc. Distillation with P_2O_5 then yields $\zeta\zeta$ -dicyano- $\beta\delta$ -dimethyloctane, b.p. 124–128°/15 mm., reduced by Na-EtOH to $\zeta\zeta$ -diamino- $\beta\delta$ -dimethyloctane (picrate, m.p. 129°), the dihydrochloride, m.p. 242° (decomp.), of which with $\text{NH}_2\cdot\text{CN}$ in hot, dry EtOH gives $\delta\delta$ -diguanidino- $\beta\delta$ -dimethyloctane dihydrochloride, decomp. 112–113° (picrate, m.p. 214–215°). This salt has no hypoglycæmic action and is not toxic, even in doses of 75 mg. per kg., to rabbits. R. S. C.

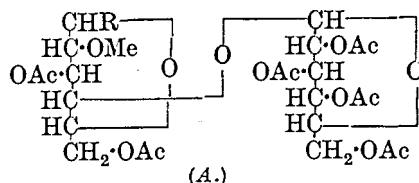
Synthesis of homoarginine. J. P. GREENSTEIN (J. Org. Chem., 1938, 2, 480–483).—Dicarbobenzyloxylysine, m.p. 104°, with PCl_5 in cold, dry CHCl_3 gives the acid chloride, converted by evaporation at 50°/vac. into the anhydride, m.p. 92°, and thence by $\text{HCl}\cdot\text{COMe}_2$ into ϵ -carbobenzyloxy-dl-lysine, m.p. 263°. Pd-hydrogenation of the Bz derivative (prepared by $\text{BzCl}\cdot\text{NaOH}$) thereof in 5N-HCl gives α -benzoyl-dl-lysine, m.p. 211°, which with $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{OMe}$ and NaOMe in MeOH gives ϵ -guanidino- α -benzoyl-dl-lysine, m.p. 273°, hydrolysed by hot 5N-HCl to ϵ -guanidino-dl-lysine [homoarginine] [sulphate, $+1\cdot5\text{H}_2\text{O}$, decomp. 127° after sintering at 112°; benzylidene derivative, m.p. 248° (decomp.)], unaffected by arginase at 40° and p_{H} 8. R. S. C.

Geometrical isomerism in the epoxynitrile series. R. GERBAUX (Bull. Acad. roy. Belg., 1938, [v], 24, 88–91).—Interaction of $\text{COMe}\cdot\text{CHMeCl}$ (I) with aq. KCN affords β -cyano- $\beta\gamma$ -oxidobutanes, b.p. 155–156°/758 mm. (35%) (II) and b.p. 142–143°/758 mm. (65%) (III). Neither affords a semicarbazone, but either with conc. HCl affords two β -chloro- α -hydroxy- α -methylbutyric acids, m.p. 75° and 92°. (II) and (III) with HCl (gas) afford isomeric γ -chloro- β -cyanobutan- β -ols, b.p. 93·4–93·6°/10 mm. (IV) and b.p. 99·8–100°/10 mm., respectively. In slightly alkaline solutions (II) and (III) afford isomeric β -cyanobutan- $\beta\gamma$ -diols, m.p. 94·4–95·4° and 107·4–108·4°, respectively. (I) with anhyd. HCN and a little KCN gives a mixture of two chlorocyanohydrins with (IV) preponderating. J. L. D.

Reactions of β -keto-nitriles with hydrogen. R. H. WILEY and H. ADKINS (J. Amer. Chem. Soc., 1938, 60, 914–918).—Partial hydrogenation of keto-nitriles, $\text{R}\cdot\text{CO}\cdot\text{CHR}\cdot\text{CN}$, in presence of Raney Ni at

35–40°/120 atm. gives 10–60% of unstable keto-amine if $\text{R} = \text{Pr}^\beta$, but not if $\text{R} = \text{Bu}^\alpha$, the nature of R' also influencing the yield. At 150–200°/270 atm. 23–58% of NH_2 -ketones are obtained with 20–40% of tetrahydropyrans and/or other products of hydrogenolysis, which often occurs extensively. At intermediate temp. indefinite products are obtained. At 130° some dialkylamine is formed. Condensation of $\text{Pr}^\beta\text{CO}_2\text{Et}$ with the appropriate nitrile by NaOEt, first at 90–100° and then at 120–130° (3–4 days), gives about 40% yields of β -keto- $\alpha\gamma$ -dimethyl-, b.p. 95–96°/24 mm., γ -methyl- α -ethyl-, b.p. 96·5°/17 mm., γ -methyl- α -n-propyl-, b.p. 91°/7 mm., and γ -methyl- α -n-butyl-valeronitrile, b.p. 128°/24 mm.; $\text{Bu}^\alpha\text{CO}_2\text{Et}$ and $\text{Bu}^\alpha\text{CN}$ give only 6% of β -keto- $\gamma\gamma$ -dimethyl- α -n-propyl-valeronitrile, b.p. 122°/12 mm. Addition of $\text{Bu}^\alpha\text{CN}$ (2 mols.) to powdered Na in boiling Et_2O gives 45% of β -imino- α -n-propyl-n-heptonitrile, b.p. 125–126°/3 mm., hydrolysed by hot 10% H_2SO_4 to β -keto- α -n-propyl-n-heptonitrile, b.p. 127°/17 mm. By hydrogenation were obtained γ -keto- δ -methyl- β -n-propyl-, m.p. 79–80°, δ -methyl- β -ethyl-, m.p. 104–105°, and $\beta\delta$ -dimethyl-n-amylamine, m.p. 140–141°, γ -hydroxy- δ -methyl-n-amylamine, b.p. 104°/23 mm. (p-nitrobenzoyl derivative, m.p. 132–133°), γ -hydroxy- $\beta\delta$ -dimethyl-n-amylamine, b.p. 105°/25 mm. (p-nitrobenzoyl derivative, m.p. 181–182°), γ -hydroxy- δ -methyl- β -ethyl-, b.p. 107°/16 mm., and n-propyl-n-amylamine, b.p. 120°/17 mm., γ -benzamido- ϵ -methyl-n-octan- δ -ol, m.p. 99–100°, δ -benzamido- ζ -methyl-n-octan- ϵ -ol, m.p. 107–108°, δ -p-nitrobenzamido-methyl-n-heptan- γ -ol, m.p. 137–138°, di- γ -ketoisohexylamine hydrochloride, m.p. 194–196°, di- $(\gamma$ -keto- β -ethylisohexylamine hydrochloride, m.p. 185–187°, cyclic ethers, $\text{C}_9\text{H}_{16}\text{O}$, b.p. 66–67°/22 mm., $\text{C}_{10}\text{H}_{18}\text{O}$, b.p. 80–81°/22 mm., and $\text{C}_{10}\text{H}_{18}\text{O}$, b.p. 88–89°/22 mm., the Bz derivative, m.p. 71·5–73·5°, of an O-free base from $\text{COPr}^\beta\cdot\text{CHPr}^\alpha\cdot\text{CN}$, and the p-nitrobenzoyl derivative, m.p. 97·5–98·5°, of an O-free base from $\text{COBu}\cdot\text{CHPr}^\alpha\cdot\text{CN}$. M.p. are corr. R. S. C.

Transformation of nitriles of the sugar series. G. ZEMPLÉN, E. BALASSA, and M. GÁRDONYI (Ber., 1938, 71, [B], 768–774).—Cellobionitrile octa-acetate (I) is transformed by $\text{HBr}\cdot\text{AcOH}$ at room temp. into cellobionamide octa-acetate (II), m.p. 164·5°, $[\alpha]_D^{25} + 32\cdot65^\circ$ in CHCl_3 , reconverted into (I) by POCl_3 at 75°. With NaOMe in MeOH (II) gives cellobionamide, hydrolysed by boiling $\text{Ba}(\text{OH})_2$ to non-cryst. cellobionic acid, isolated as the Ca salt. Similarly gluconamide penta-acetate gives gluconamide, m.p. 145–145·5°, $[\alpha]_D^{25} + 31\cdot11^\circ$ in H_2O . Galactonitrile penta-acetate is converted by $\text{HBr}\cdot\text{AcOH}$ into galactonamide penta-acetate, m.p. 177–177·5°, $[\alpha]_D^{25} + 26\cdot80^\circ$ in CHCl_3 , whence galactonamide, m.p. 170–



171°. Acetobromocellobiose and AgCN in boiling xylene yield cellobiosido-1-nitrile hepta-acetate (III)

(4; R = ON), m.p. 172·5°, $[\alpha]_D^{25}$ -6·25° in CHCl_3 , converted by AgOAc and Ac_2O at 100° into β -cellobiose octa-acetate, m.p. 194°, $[\alpha]_D^{25}$ -12·58° in CHCl_3 , and hydrolysed by boiling $\text{Ba}(\text{OH})_2$ to non-cryst. *cellobiosido-1-carboxylic acid*, isolated as the *Ca* salt. $\text{HBr}\cdot\text{AcOH}$ and (III) afford *cellobiosido-1-carboxylamide*, m.p. 189°, $[\alpha]_D^{25}$ +0·84° in CHCl_3 , converted by $\text{NH}_3\cdot\text{H}_2\text{S}$ in EtOH at 70° into *cellobiosido-1-thiocarboxylamide hepta-acetate*, m.p. 188—189°, $[\alpha]_D^{25}$ $\pm 0^\circ$ in CHCl_3 . H. W.

Change in optical rotation of gluconitrile. P. E. PAPADAKIS and H. J. COHEN (J. Amer. Chem. Soc., 1938, 60, 765—768).—The forms, m.p. 145° and 120·5°, of gluconitrile are obtained by crystallising from AcOH or abs. EtOH , respectively. The former has $[\alpha]_D +9\cdot96^\circ$ (const.) in H_2O , +6·27° in $\text{C}_5\text{H}_5\text{N}$. The latter has $[\alpha]_D +6\cdot03^\circ$ in $\text{C}_5\text{H}_5\text{N}$, about +10° in H_2O , changing first to a negative and then again to a small positive val. The m.p. of mixtures is intermediate. R. S. C.

Phosphorus analogues and homologues of choline and betaine. Onium compounds. XVII. R. R. RENSHAW and R. A. BISHOP (J. Amer. Chem. Soc., 1938, 60, 946—947; cf. A., 1937, II, 488).— PMe_3 and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ in abs. EtOH at 90—100° give *trimethyl- β -hydroxyethylphosphonium chloride*, hygroscopic. $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{PMe}_3\text{Br}$ and hot $\text{KOH}\cdot\text{EtOH}$ (1 mol.) give PMe_3 and *ethylenebis(trimethylphosphonium bromide)*. PET_3 (prep. in 70% yield by the Grignard reagent) with $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{OH}$ at 50°, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{OAc}$ at 40°, or $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ at room temp., yields *triethyl- β -hydroxyethyl-*, m.p. 223° (corr.), *triethyl- β -acetoxyethyl-*, m.p. 74·6° (corr.), and *carboethoxymethyltriethyl-phosphonium bromide*, m.p. 83·2° (corr.), respectively. Very little PMe_3 is obtained by the Grignard reaction. R. S. C.

Separation of α - and β -lecithin.—See A., 1938, III, 546.

Co-ordination of silver ion with unsaturated compounds. S. WINSTEIN and H. J. LUCAS (J. Amer. Chem. Soc., 1938, 60, 836—847).—By the distribution technique (A., 1937, I, 135) $\text{CHMe}\cdot\text{CMe}_2$, Δ^8 -pentene, Δ^8 -hexene, *cyclohexene*, $\text{CHMe}\cdot\text{CHPh}$, $(\text{CHMe}\cdot\text{CH})_2$, $(\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)_2$ (I), $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$, $\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$, and PhOH are shown to co-ordinate with Ag^+ . (I) and dicyclopentadiene give solid compounds with AgNO_3 . Equilibrium consts. are measured. *cis*- and *trans*- Δ^8 -Butene are not equilibrated by Ag^+ . The resulting co-ordination compounds are assigned resonance formulæ and similar structures are assigned to compounds of unsaturated substances with, e.g., Pt, Al, Fe, and Zn salts, Fe carbonyls, and NO_2 -compounds. Cd, Co, Cr, Cu, Fe, Ni, Pb, Tl, and Zn ions do not co-ordinate. R. S. C.

Kinetics of the formation of the Grignard reagent. I. M. KILPATRICK and H. P. SIMONS (J. Org. Chem., 1938, 2, 459—469).—Reaction of Mg with EtBr is induced by contact with other substances. An apparatus is described in which a Mg cylinder in contact with glass is stirred with $\text{EtBr}\cdot\text{Et}_2\text{O}$. The rate of reaction $\propto [\text{EtBr}]$ after an induction period during which C_4H_{10} , but no MgEtBr , is formed. I

decreases the induction period, but has no effect on the subsequent reaction rate. R. S. C.

Co-ordination compounds of palladous chloride. M. S. KHARASCH, R. C. SEYLER, and F. R. MAYO (J. Amer. Chem. Soc., 1938, 60, 882—884).—Reaction of PdCl_2 with PhCN yields $(\text{PhCN})_2\cdot\text{PdCl}_2$, from which compounds containing 1 mol. of C_2H_4 , isobutene, *cyclohexene* (I), or styrene (II) per mol. of PdCl_2 have been obtained by the action of C_2H_4 derivatives. The compounds appear to be bimol.; a general structural formula has been proposed. The stability decreases in the order (I), C_2H_4 , (II). E. S. H.

Organic chemistry of gold and production of gold mirrors. C. S. GIBSON (Compt. rend. XVII Cong. Chim. Ind., 1937, 877—880).—A summary of work previously published by Gibson and collaborators. F. N. W.

Complex compounds of platinum metals with thio-, seleno-, and telluro-ethers.—See A., 1938, I, 322.

Homologues of cyclopropane. Methylcyclopropane. I. Preparation. W. A. LOTT, W. G. CHRISTIANSEN, and L. F. SHACKELL (J. Amer. Pharm. Assoc., 1938, 27, 125—128).—Reduction of $\alpha\gamma$ -dibromobutane with Zn in 85% EtOH affords methylcyclopropane (yield 81%, isobutylene content 0·68%); similar reduction of $\alpha\gamma$ -dichloroisobutane yields practically pure isobutylene. The reduction products of various dihalogeno-propanes and -butanes are discussed. F. O. H.

Catalytic dehydrogenation of cyclohexane in presence of oxides of chromium and vanadium. H. S. TAYLOR and L. M. YEDDANAPALLI (Bull. Soc. chim. Belg., 1938, 47, 162—171).—The Cr_2O_3 is obtained as a hard, black, vitreous gel by boiling a solution of $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ with NH_4OAc , cooling, adding NH_3 , and again boiling. The product is washed with H_2O ; dried at 100—300°, and then heated *in situ* in H_2 at 400°. The activity of the catalyst in the dehydrogenation of *cyclohexane* at 383—444° is reproducible. The gas evolved contains >95% of H_2 . The apparent energy of activation is 24 kg.-cal. per mol. V_2O_5 is obtained by slowly evaporating a solution of NH_4VO_3 and $\text{H}_2\text{C}_2\text{O}_4$ to dryness, gradually raising the temp. of the residue to 400°, and reducing the product in H_2 *in situ* at 400°. It is inferior to Cr_2O_3 as catalyst. Mixtures of Cr_2O_3 and U_2O_3 are intermediate in activity; their apparent energies of activation are of the same order as those of Cr_2O_3 . It is suggested that in the case of catalytic gels of Cr_2O_3 the energy of desorption of H determines the magnitude of the observed energy of activation. H. W.

Thermal decomposition of alicyclic compounds. I. Decomposition of cyclohexane and some simpler hydrocarbons. F. O. RICE, P. M. RUOFF, and E. L. RODOWSKAS (J. Amer. Chem. Soc., 1938, 60, 955—961).—Investigations designed to isolate the primary products of thermal decomp. are best conducted at low pressures, which retard subsequent bimol. reactions and polymerisation without affecting the rate of the unimol. thermal decomp. A

suitable technique is described. At 700–800°/7–15 mm. *cyclohexene* (I) gives 90–95% of C_6H_4 and butadiene (II) with 1–2% each of $C_6H_6+2H_2$ and $2C_2H_4+C_2H_2$, but no tar. C_2H_4 and (II) are unaffected under the conditions used, and C_2H_6 and C_4H_{10} are barely affected. (I) slowly removes a Te mirror, giving an unstable compound, but $COMe_2$ gives free radicals much more easily. *cyclohexane* and (II) give only traces of free radicals. Dissociation of (I) is assumed to occur by way of the radical,

$-CH_2\cdot[CH_2]_2\cdot\dot{C}H\cdot CH\cdot CH_2$, i.e., the resonance form common to $-CH_2\cdot[CH_2]_2\cdot\dot{C}H\cdot CH\cdot CH_2-$ and

$-CH_2\cdot[CH_2]_2\cdot\dot{C}H\cdot CH\cdot CH_2$, this radical being formed in preference to others possible because resonance involves the least energy change and is possible only with this mode of fission; C_2H_4 and (II) are then formed by simple electronic shift. Similarly decomp. of dipentene to isoprene occurs by way of $CH_2\cdot CMe\cdot CH\cdot CH_2\cdot CH(CMe\cdot CH_2)\cdot CH_2-$, and that of α -pinene to *allocimene* by way of

$\begin{array}{c} H \\ \diagup \\ CMe_2 \end{array} > C < \begin{array}{c} CH_2\cdot\dot{C}H \\ CH_2\cdot\dot{C}H \end{array} > CMe \text{ and ocimene.}$

R. S. C.

Action of aluminium chloride on cyclohexylbenzene. B. B. CORSON and V. N. IPATIEV (J. Amer. Chem. Soc., 1938, 60, 747–749).—With $AlCl_3$ at 80–85° *cyclohexylbenzene* decomposes to (a) C_6H_6 and $C_6H_4(C_6H_{11})_2$ and (b) $C_6H_{10}Ph_2$ and C_6H_{12} . The products isolated were C_6H_6 , *cyclohexane*, a mixture of hexane and (?) methylcyclopentane, 1:4-diphenylcyclohexane (I), m.p. 169–170°, and a liquid mixture (II) thereof with the 1:3-isomeride, and a hydrocarbon, $C_{24}H_{30}$, b.p. 330–370°/2 mm. (hydrogenated by H_2-Ni at 240°/100 kg. per sq. cm. to a liquid *tricyclohexylcyclohexane*). Hydrogenation of (II) gives 1:4- and 1:3-dicyclohexylcyclohexane, m.p. 62.5–63.5°, the latter product being also prepared from $m-C_6H_4Ph_2$ and H_2-Ni . Hydrogenation of $o-C_6H_4Ph_2$ gives 1:2-dicyclohexylcyclohexane, m.p. 44.5–46°. Identity of (I) with Kursanov's product (A., 1902, i, 20) and that from C_6H_6 -*cyclohexene*- $AlCl_3$ is proved.

R. S. C.

Reaction of cycloparaffins with aromatic hydrocarbons. Decycloalkylation. A. V. GROSSE and V. N. IPATIEV (J. Org. Chem., 1938, 2, 447–458).—"Decycloalkylation," i.e., alkylation of aromatic hydrocarbons by cycloparaffins, is effected in presence of metallic catalysts. The ease and uniformity of reaction depend on the nature of the reactants. In presence of $AlCl_3$ cyclopropane converts C_6H_6 at <0° or 25–30° into *n*-propylbenzenes up to *hexa-n-propylbenzene*, m.p. 103°, b.p. 332° (photomicrograph); reaction does not occur by way of propylene, which gives Pr^{β} -compounds and none higher than $C_6H_2Pr^{\beta}_4$. Methylcyclobutane gives mixed amylbenzenes, including *iso*amylbenzene, with some *iso*- C_5H_{12} and Ph_2 . *cyclopentane* reacts only at 150°, the main reaction products, amylbenzenes, being contaminated with products of dealkylation, e.g., $PhMe$ and $PhEt$, and of side-reactions, e.g., *cyclopentylbenzene*. In presence of $ZrCl_4$ 2- $C_{10}H_7Me$ and cyclopropane at 30–35° give methylpropylnaphthalenes, b.p. 136–138°/9.5 mm., and higher products.

R. S. C.

Velocity of hydrogenation of aromatic hydrocarbons.—See A., 1938, I, 317.

Hydrogen fluoride as a condensing agent. J. H. SIMONS and S. ARCHER (J. Amer. Chem. Soc., 1938, 60, 986).—In presence of HF at 0° C_6H_6 with C_3H_6 gives $PhPr^{\beta}$, with $Pr^{\beta}Cl$ gives (?) $C_6H_4Pr^{\beta}_2$, with *iso*- C_4H_8 or Bu^iCl gives $PhBu^i$ and $PhBu^i_2$, and with $CMc_2\cdot CHMe$ or CMc_2EtCl gives products, b.p. 188° and 262–265°, respectively.

R. S. C.

Fluorinated derivatives of methane bearing phenyl groups. A. L. HENNE and H. M. LEICESTER (J. Amer. Chem. Soc., 1938, 60, 864–865).— CPh_2Cl_2 and SbF_3 with or without a little Br at 140° give *difluorodiphenylmethane*, b.p. 125°/10 mm., about 260° (decomp.)/760 mm., m.p. –1.9° to 1.8°, which is more stable than $CHPhF_2$, but less so than $CPhF_3$. CCl_2F_2 , C_6H_6 , and $AlCl_3$ give HF, $CHPh_3$, and $CPh_3\cdot OH$, derived by decomp. of CPh_3Cl . Ph decreases the stability of $>CF_2$ and $\cdot CF_3$.

R. S. C.

Additive products of benzene derivatives and halogen. IX. Nitrobenzene and chlorine. T. VAN DER LINDEN (Rec. trav. chim., 1938, 57, 342–344).— $PhNO_2$ and liquid Cl_2 in a sealed tube in sunlight for about 6 months afford 1:2:3:4:5:6-hexachloro-1-nitrocyclohexane, m.p. 212–213°; after 7 months, β - $p-C_6H_4Cl_2\cdot Cl_6$ (?) (decomposed with $KOH-EtOH$ to C_6HCl_5), ennea- and hepta-chlorocyclohexane (possibly) are obtained.

A. T. P.

Liquid-vapour equilibria of binary systems of nitrotoluenes.—See 1938, A., I, 313.

Preparation of o-dinitro-compounds. R. KUHN and W. VAN KLAVEREN (Ber., 1938, 78, [B], 779–780).— $o-(NO_2)_2$ -Compounds are advantageously obtained by the action of a warm mixture of HNO_3 (d 1.4) and 30% H_2O_2 on *o*-nitronitroso-derivatives in $AcOH$. The active reagent is probably a peracid since the separate components react much less rapidly. 4:5-Dinitro-*o*- and -*m*-xylene, 2:3-dinitro-5:6:7:8-tetrahydronaphthalene, and 2:3-dinitrohydrindene are obtained in 75%, 78%, 88%, and 62% yield, respectively.

H. W.

Cationoid reactivity of aromatic compounds. V. Fission of arylsulphones by means of sodamide and piperidine. W. BRADLEY (J.C.S., 1938, 458–460; cf. Bradley *et al.*, A., 1932, 622).—When heated with $NaNH_2$ and piperidine, Ph_2SO_2 yields 1-phenylpiperidine (I) (*p*-chlorobenzeneazo-derivative, m.p. 143°) and $PhSO_2H$, $PhSO_2\cdot CH_2Ph$ yields (I) and $CH_2Ph\cdot SO_2H$, while *p*- $MeSO_2\cdot C_6H_4Me$ yields 1-*p*-tolylpiperidine and $MeSO_2H$ (characterised as $MeSO_2\cdot CH_2Ph$). Even in presence of O_2 , no nuclear substitution occurs. $(CH_2Ph)_2SO_2$ does not undergo fission.

A. LI.

Diphenyl series. XI. Nitration of some 2:4' diphenyl derivatives. C. FINZI and V. BELLAVITA (Gazzetta, 1938, 68, 77–87).—2:4'-(C_6H_4Br) $_2$ is nitrated ($EtNO_3$, KNO_3 , or HNO_3 in H_2SO_4) to a mixture converted by $C_5H_{11}N$ into 2-bromo-4:3'-dinitro-4'-piperidyldiphenyl, m.p. 130–131°, and 5:3'-dinitro-2:4'-dipiperidyldiphenyl, m.p. 121°; these are also obtained from the dibromodinitro-

diphenyls (A., 1933, 388). With $\text{H}_2\text{SO}_4\text{-EtNO}_3$, 4':2- $\text{C}_6\text{H}_4\text{Br-C}_6\text{H}_4\text{NO}_2$ gives 4'-bromo-2:3'-dinitrodiphenyl, m.p. 148°, which with $\text{C}_5\text{H}_{11}\text{N}$ yields 2:3'-dinitro-4'-piperidylidiphenyl, m.p. 88–89°. 2:4'- $\text{C}_6\text{H}_4\text{Br-C}_6\text{H}_4\text{NO}_2$ and $\text{H}_2\text{SO}_4\text{-EtNO}_3$ give 2-bromo-5:4'-dinitrodiphenyl, m.p. 164–165°, converted into 5:4'-dinitro-2-piperidylidiphenyl, m.p. 155°. 2:4'- $\text{NO}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-NH}_2$ and $\text{H}_2\text{SO}_4\text{-EtNO}_3$ give 2:4'-dinitro-4'-aminodiphenyl, m.p. 138–139° (Ac derivative, m.p. 186°) [converted into 2:4- $\text{C}_6\text{H}_3\text{Ph}(\text{NO}_2)_2$], and 2:2'-dinitro-4'-aminodiphenyl, m.p. 138–139° (converted into 2:2'- $\text{NO}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-NO}_2$). 4':2- $\text{NO}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-NH}_2$ yields 4:4'-dinitro-2-aminodiphenyl, m.p. 208° (Ac derivative, m.p. 168–169°) (converted into 4:4'- $\text{NO}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-NO}_2$). 2:4'- $\text{NO}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-NHAc}$ gives 2:3'-dinitro-4'-acetamidodiphenyl, m.p. 160–161°, reduced and acetylated to 2:3':4'- $\text{NHAc-C}_6\text{H}_4\text{-C}_6\text{H}_3(\text{NHAc})_2$. E. W. W.

Cumulenes. I. Synthesis of tetraphenylhexapentaene and di-diphenylhexapentaene. R. KUHN and K. WALLENFELS (Ber., 1938, 71, [B], 783–790).—Cumulenes are compounds with an unbroken sequence of C:C linkings whereas the term polyenes is reserved for substances with conjugated double linkings. Tetraphenylbutenediol in Et_2O is transformed by P_2I_4 into $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^{\alpha\beta\gamma}$ -butatriene, m.p. 236.5–237°. Successive addition of $\text{CH}_2\text{:C:C:CH}$ and COPh_2 to MgEtBr in Et_2O yields $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\beta\delta}$ -hexadi-inene- $\alpha\zeta$ -diol, m.p. 140–141°, converted by P_2I_4 in $\text{C}_5\text{H}_5\text{N}$ at 0° into $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\alpha\beta\gamma\delta}$ -hexapentaene, $\text{CPh}_2\text{:C:C:C:C:CPh}_2$, m.p. 302° after softening at 290°. It forms scarlet crystals which are not fluorescent when solid or in solution. It gives a brown colour with SbCl_3 in CHCl_3 but does not react with $\text{C}(\text{NO}_2)_4$. It is remarkably stable towards O_3 but immediately decomposed by O_3 . It readily adds Br and I. It is scarcely affected by KMnO_4 in $\text{C}_5\text{H}_5\text{N}$ at 20°. It does not add maleic anhydride or *p*-benzoquinone. It is unchanged by Zn dust in CHCl_3 but immediately becomes decolorised on addition of AcOH . With a mild catalyst (PdO) the five double linkings become saturated without affecting the Ph residues whereby the transitory occurrence of an intense green fluorescence is remarkable. Analogously fluorenone affords $\alpha\zeta$ -di-diphenylene- $\Delta^{\beta\delta}$ -hexadi-inene- $\alpha\zeta$ -diol, colourless leaflets, m.p. 257°. This with P_2I_4 affords $\alpha\zeta$ -di-diphenylenehexapentaene, m.p. 441–442°, the almost black crystals of which give solutions comparable with KMnO_4 in colour. It is not fluorescent. Its solutions in CHCl_3 are unchanged by exposure to bright sunlight. With an equal no. of double linkings the absorption of light is displaced more towards longer λ by cumulated than by conjugated double linkings. H. W.

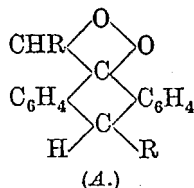
Preparation of 1:2:7-trimethyl-4-isopropylindene and 1:2:7-trimethyl-4-isopropylhydrindene. C. L. CARTER and S. N. SLATER (J.C.S., 1938, 546).—2:7-Dimethyl-4-isopropyl-1-hydrindene (Cook *et al.*, A., 1935, 74) with MgMeI gives 1:2:7-trimethyl-4-isopropylindene, b.p. 154–157°/17 mm., reduced (Pd-norit) to the -hydrindene, b.p. 154–155°/29 mm. A. Li.

Synthesis of 1:1:2:6-tetramethyl-1:2:3:4-tetrahydronaphthalene. Constitution of irene. M. T. BOGERT and P. M. APFELBAUM (J. Amer. Chem. Soc., 1938, 60, 930–933).—Diagnosis of irene as 1:1:2:6-tetramethyl-1:2:3:4-tetrahydronaphthalene (I) (Ruzicka *et al.*, A., 1933, 1297) is confirmed by synthesis. Oxidation of irene proceeds with loss of 1 C; analogies are cited. $m\text{-C}_6\text{H}_4\text{Me}[\text{CH}_2]_2\text{OH}$ [from $m\text{-C}_6\text{H}_4\text{Me-MgBr}$ and $(\text{CH}_2)_2\text{O}$], b.p. 115–118°/10 mm. (phenylurethane, m.p. 59–60°), with PBr_3 gives the bromide, b.p. 103–106°/10 mm., the Grignard reagent from which with COMePr^{δ} gives ϵ -*m*-tolyl- $\alpha\gamma$ -dimethyl-*n*-pentan- γ -ol, b.p. 150–152°/10 mm., which with hot H_2SO_4 gives (I), b.p. 120–125°/10 mm. (physical data = those of irene). With Se at 250–280° it gives 1:2:6- $\text{C}_{10}\text{H}_5\text{Me}_3$. With CrO_3 it gives α -2-carboxy-*p*-tolylisopropyl Me ketone, m.p. 154–155° [= “trihydroxydehydroirene” (Tiemann *et al.*, A., 1894, i, 80; 1895, i, 530)], which with NaOHal gives impure α -2-carboxy-*p*-tolylisobutyric acid. With KMnO_4 (I) gives α -2:4-dicarboxyphenylisobutyric [“ionisgentricarboxylic”] acid [anhydride, m.p. 214° (corr.)]. R. S. C.

Synthetic experiments with polyterpenes. W. HUBER (Ber., 1938, 71, [B], 725–734).—The prep. of hydronaphthalene or hydrophenanthrene derivatives with the conjugated linkings in a single ring is difficult by reason of the sensitiveness of these compounds to heat and traces of acid. 2-Keto-10-methyl- $\Delta^{1:9}$ -octahydronaphthalene is reduced by $\text{Al}(\text{OPr}^{\delta})_3$ and $\text{Pr}^{\delta}\text{OH}$ to 2-hydroxy-10-methyl- $\Delta^{1:9}$ -octahydronaphthalene (I), b.p. 68°/0.18 mm. [non-cryst. benzoate (II); dinitrobenzoate, m.p. 69–69.5°]. When heated at 170° in presence of air (II) gives BzOH and an oil which resinifies with change in absorption spectrum when kept in air. The only homogeneous product which can be obtained by loss of BzOH from (II) in N_2 alone or in presence of CaCO_3 or KOH or by loss of H_2O from (I) is 10-methyl- $\Delta^{8:9-1:2}$ or $\Delta^{7:8-9:1}$ -hexahydronaphthalene, b.p. 142°/12 mm., which does not add maleic anhydride (III); the production of 10-methyl- $\Delta^{1:9-2:3}$ -hexahydronaphthalene is shown by the absorption spectrum of the crude product and the formation of an adduct, $\text{C}_{15}\text{H}_{20}\text{O}_4$, b.p. 172°/12 mm., with (III). Addition of cyclohexanone and 2-acetyl-1-methyl- Δ^1 -cyclohexene in $\text{C}_5\text{H}_5\text{N}$ to KOPr^{δ} in Et_2O affords 9-keto-13-methyl- $\Delta^{10:11}$ -dodecahydronaphthalene, b.p. 81°/10⁻⁴ mm. [2:4-dinitrophenylhydrazones, m.p. 103–104°; semicarbazone, m.p. (indef.) 116–118°], reduced by $\text{Al}(\text{OPr}^{\delta})_3$ in $\text{Pr}^{\delta}\text{OH}$ to 9-hydroxy-13-methyl- $\Delta^{10:11}$ -dodecahydronaphthalene (IV), b.p. 79°/0.007 mm. (non-cryst. benzoate (V); dinitrobenzoate, m.p. 97.5–98°). Elimination of H_2O from (IV) or of BzOH from (V) invariably yields a mixture of hydrocarbons. 13-Methyl- $\Delta^{9:14-10:11}$ -decacydronaphthalene, its adduct, $\text{C}_{19}\text{H}_{26}\text{O}_4$, b.p. 220°/12 mm., from (III), and 13-methyl- $\Delta^{9:10-11:12}$ -decacydronaphthalene, b.p. 76.5°/1 mm., are described. H. W.

Dissociable anthracene oxides. Influence of meso aliphatic groups. A. WILLEMART (Bull. Soc. chim., 1938, [v], 5, 556–564).—Partly a review of work already noted (A., 1938, II, 50). The oxides of 9-methyl- (I), 9-ethyl- (II), 9:10-dimethyl-, and

9-methyl-10-ethyl-anthracene (III), prepared in CS_2 , are described. That of (I) decomposes violently at about 80° , the others at indefinite temp. Insolations of (I) and (II) in Et_2O gives *polymerides*, m.p. $>250^\circ$ (block) and about 275° (block), respectively. The differing amounts of O_2 evolved when alkyl-, 9-aryl-10-alkyl, and 9:10-diaryl-anthracene oxides are heated



are due to the stabilisation of anthracene by aryl towards oxidation and not to a difference in formula, e.g., (A) for alkyl oxides. Thus, all the hydrocarbons have the normal absorption of anthracene derivatives in the ultra-violet, and (III) gives only one oxide.

R. S. C.

Preparation and photochemical oxidation of 2:4-cholestadiene. E. L. SKAU and W. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 986–987).—Conversion of cholesterol into 2:4-cholestadiene, m.p. 68.5° , $[\alpha]_D^{25} +168.5^\circ$ in Et_2O , is modified to give a 30% yield. Previous material contained cholesteryl-ene. With O_2 in presence of eosin and light the diene gives a stable *peroxide*, $\text{C}_{27}\text{H}_{44}\text{O}_2$, m.p. 118.5 – 120.5° , $[\alpha]_D^{25} +52.8^\circ$ in CHCl_3 .

R. S. C.

Production of methylcholanthrene from cholic acid. C. SANNIÉ (Bull. Soc. chim., 1938, [v], 5, 260–261).—The method of Fieser and Newman (A., 1935, 859) is simplified: cholic acid is acetylated, and the crude product oxidised (CrO_3 - AcOH) to 12-keto-3:7-diacetoxycholanic acid (A., 1933, 158), which by pyrolysis and Se gives methylcholanthrene.

E. W. W.

Reduction and hydrogenation of methylcholanthrene. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1938, 60, 940–946).—The so-called 6:7:17:20:22:23-hexahydromethylcholanthrene, m.p. 160 – 160.5° , of Wieland and Dane (A., 1933, 1161) is the 1:2:3:4:11:14- H_6 -derivative (I), for with anhyd. $\text{Na}_2\text{Cr}_2\text{O}_7$ - AcOH it gives 6-methyl-1':2':3':4'-tetrahydro-1:2-benzanthraquinone-5-acetic acid, m.p. 283 – 284° (decomp.), which gives a vat test and is reduced by Zn dust- Cu -aq. NH_3 to 1':2':3':4'-tetrahydro-1:2-benzanthracene-5-acetic acid, m.p. 267 – 269° (decomp.). Attempts to re-form the cholanthrene ring system failed. Hydrogenation of methylcholanthrene (II) [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ additive compound, m.p. 203.5 – 204°] is slow; partial or complete hydrogenation in presence of PtO_2 -Pd in EtOAc - AcOH gives a mixture of (I) and the 6:7- H_2 -compound (III), m.p. 154.5 – 155° [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ additive compound, m.p. 153.4 – 154.5°], which indicates a dual mode of reaction. Structures assigned are confirmed by absorption spectra, which are detailed on a new system for (I), (II), (III), cholanthrene, 11:14-dihydromethylcholanthrene, new m.p. 138 – 139° , 10-methyl-1':2':3':4'- and -5:6:7:8-tetrahydro-1:2-benzanthracene, C_{10}H_8 , phenanthrene, anthracene, and 2- $\text{C}_{10}\text{H}_7\text{Ph}$, m.p. 102.2 – 102.7° .

R. S. C.

Polycyclic aromatic hydrocarbons. XVII. Completion of the synthesis of the twelve monomethyl-1:2-benzanthracenes [and synthesis of 4-isopropylchrysene]. J. W. COOK and A. M. G** (A., II.)

ROBINSON (J.C.S., 1938, 505–513).—Anthracene, $(\text{CH}_2\text{CO})_2\text{O}$, and AlCl_3 in PhNO_2 yield a mixture of isomerides containing β -2-anthroylpropionic acid, m.p. 220 – 221° (*Me* ester, m.p. 144.5 – 145.5°), which is oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$, then KMnO_4) to anthraquinone-2-carboxylic acid, and is reduced (Clemmensen) to γ -2-anthrylbutyric acid, m.p. 194 – 195° , cyclised by SnCl_4 or AlCl_3 to 1'-keto-1':2':3':4'-tetrahydro-1:2-benzanthracene, m.p. 114 – 114.5° . MgMeI converts this into a carbinol which when boiled with picric acid in EtOH gives the *picrate*, m.p. 120 – 121° , of 1'-methyl-3':4'-dihydro-1:2-benzanthracene, m.p. 74 – 75° . Dehydrogenation (Pt-black) of this yields 1'-methyl-1:2-benzanthracene, m.p. 137.5 – 138.5° (*di-picrate*, m.p. 119° ; *quinone*, m.p. 188.5 – 189.5°). $(\text{CH}_2)_2\text{O}$ and 1:4:6- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{MgBr}$ in Et_2O yield β -4-methoxy-m-tolylethyl alcohol, m.p. 45 – 46° ; the Grignard compound of the corresponding chloride, b.p. 126 – 127° , reacts with *trans*- β -decahydronaphthalene in Et_2O and PhOMe , giving a carbinol, the 3:5-dinitrobenzoate, m.p. 117 – 117.5° , of which when dehydrated (KHSO_4) affords 2- β -(4'-methoxy-m-tolyl)ethyl- $\Delta^{2,3}$ -octahydronaphthalene, b.p. 178 – $180^\circ/0.5$ mm., cyclised by AlCl_3 in CS_2 to 4'-methoxy-1'-methyl-1:2-benzanthracene, m.p. 80.5 – 81° . The *OMe* could not be removed. 8-Methyl-1:2-benzanthracene (II): 3-acetylphenanthrene condenses (*Na*) with *Et* succinate giving methyl-3-phenanthryl-itaconic acid, m.p. 192 – 193° (*anhydride*, m.p. 203°), reduced by *Na*-*Hg* to α -(α -3-phenanthryl)ethyl-succinic acid, m.p. 183° (*anhydride*, m.p. 145°), cyclised by AlCl_3 in PhNO_2 to a mixture of 5-keto-8-methyl-5:6:7:8-tetrahydro-1:2-benz-7-anthracic acid, m.p. 214 – 215° [*semicarbazone*, m.p. 275° (decomp.)], and -benz-7-phenanthroic acid, m.p. 177 – 178° (ratio 10:1). Reduction (Clemmensen) of the former acid yields 8-methyl-5:6:7:8-tetrahydro-1:2-benz-7-anthracic acid, m.p. 215 – 217° , which with Pt-black at 300° gives (II), m.p. 107° [*picrate*, m.p. 161 – 162° ; $\text{s}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3$ complex, m.p. 164 – 165° ; *quinone*, m.p. 191 – 192°]. 1- $\text{C}_{10}\text{H}_7\text{Me}$, α - $\text{C}_{10}\text{H}_7\text{COCl}$, and AlCl_3 in CS_2 yield 4-methyl-1:1'-dinaphthyl ketone, m.p. 100 – 101.5° (*picrate*, m.p. 86 – 87.5°); both this and the 2-Me ketone, when heated with AlCl_3 and *NaCl*, give 3-methyl-1:2:5:10-dibenz-9-anthrone, m.p. 221° . Oxidation of this (CrO_3) gives 3-methyl-1:2-benzanthraquinone-5-carboxylic acid, m.p. 305 – 306° , reduced (SnCl_2 in HCl followed by *Zn* + *NaOH*) to 3-methyl-1:2-benz-5-anthracic acid, m.p. 320 – 322° (decomp.) (*Me* ester, m.p. 170 – 171°), which with *Cu*-bronze in 'quinoline' affords 3-methyl-1:2-benzanthracene (*picrate*, m.p. 153°).

1- $\text{C}_{10}\text{H}_7\cdot[\text{CH}_2]_2\cdot\text{MgCl}$ and tetrahydrocarvone in Et_2O yield a carbinol which when dehydrated (KHSO_4) gives 2-methyl-1-(β -1'-naphthylethyl)-5-isopropyl- Δ^1 -cyclohexene, b.p. 160 – $165^\circ/0.15$ mm., cyclised by AlCl_3 in CS_2 to methylisopropyl-octahydrochrysene, m.p. 108° . This is converted by *Se* at 320° into 4-isopropylchrysene, m.p. 227° (2:7-dinitroanthraquinone complex, m.p. 241 – 242°). *Et* α -methyl- δ -isopropyl-pimelate, b.p. $110^\circ/0.5$ mm. (from tetrahydrocarvone; cf. Simonsen *et al.*, A., 1935, 755), with *Na* in *PhMe* yields *Et* 6-methyl-3-isopropylcyclohexanone-2-carboxylate, b.p. $100^\circ/0.2$ mm., the *K* compound of which does not condense with 1- $\text{C}_{10}\text{H}_7\cdot[\text{CH}_2]_2\cdot\text{Cl}$. A. LI.

Synthesis of perylene from anthracene. I. J. POSTOVSKI and N. P. BEDNJAGINA (J. Gen. Chem. Russ., 1937, 7, 2919—2925).—Anthracene, aq. CH_2O , and HCl afford 9:10-di(chloromethyl)anthracene, m.p. 263—264° (decomp.), which with $\text{CHNa}(\text{CO}_2\text{Et})_2$ in boiling xylene yields 9:10-di-($\beta\beta$ -dicarbethoxyethyl)anthracene, m.p. 171°, hydrolysed by NaOH in EtOH to the corresponding acid, m.p. 244—246° (compound with maleic anhydride, m.p. 280°). This, when heated at 250—265°/10 mm., affords 9:10-di-(β -carboxyethyl)anthracene, m.p. 244° (compound with maleic anhydride, m.p. 306°), which with SOCl_2 gives the corresponding acid chloride, m.p. 168—170°. This is heated at 50—60° with AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$, to yield 3:9-diketol:1:2:7:8-tetrahydroperylene, m.p. 338—340° (decomp.), from which 3:9-diacetoxy-1:7-dihydroperylene, m.p. 280°, is obtained with Ac_2O in $\text{C}_5\text{H}_5\text{N}$ (12 hr. at room temp.), and perylene by distillation from Zn dust. R. T.

Symmetrical derivatives of chrysene. I. G. R. RAMAGE (J.C.S., 1938, 397—400; cf. A., 1933, 828).— $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$, prepared from $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHO}$, MeOAc , and Na , is reduced by Al-Hg in Et_2O to $p\text{-C}_6\text{H}_4\text{Me}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{Me}$ and *Me* $\beta\gamma$ -di-*p*-tolyladipate-a, m.p. 150° [corresponding acid-a (I), m.p. 320°], and crude isomeride-b (II), probably the *meso*- and *r*-forms, respectively, separable by means of Et_2O . Ring-closure of (I) is effected by hot H_2SO_4 (85%, 3 hr.) or by successive treatment with SOCl_2 and then $\text{AlCl}_3\text{-C}_2\text{H}_2\text{Cl}_4$ (60°, 12 hr.), giving 2:11-diketo-5:14-dimethyl-1:2:9:10:11:18-hexahydrochrysene-a, m.p. 312° (decomp.), reduced (Clemmensen) to 5:14-dimethyl-1:2:9:10:11:18-hexahydrochrysene-a (III), m.p. 140°. Similarly, (II) is converted into 2:11-diketo-5:14-dimethyl-1:2:9:10:11:18-hexahydrochrysene-b, m.p. 201—202°, reduced to 5:14-dimethyl-1:2:9:10:11:18-hexahydrochrysene-b, m.p. 108°. Dehydrogenation (Se, 6 hr., 280—320°) of both this and (III) gives 5:14-dimethylchrysene, m.p. 218° [*s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 195°; styphnate, m.p. 204°; picrate, m.p. 171—172°]. *cis*-Diketohexahydrochrysene (*loc. cit.*) gives a dihydrazone, decomp. about 120°, which when heated with NaOEt-EtOH (15 hr., 180°) gives *cis*-hexahydrochrysene identical with that obtained by Clemmensen reduction. Similarly the dihydrazone, m.p. 360°, of *trans*-diketohexahydrochrysene gives *trans*-hexahydrochrysene. Reduction of $\text{CPhMe}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ with Al gives $\text{CHPhMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ and *Me* $\beta\gamma$ -diphenyl- $\beta\gamma$ -dimethyladipate-a, m.p. 134°, together with the crude isomeride-b (IV). The former with hot $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ (3 hr.) gives 2:11-diketo-9:18-dimethyl-1:2:9:10:11:18-hexahydrochrysene-a, m.p. 256°, the dihydrazone of which with NaOH-EtOH (as above) gives 9:18-dimethyl-1:2:9:10:11:18-hexahydrochrysene-a, m.p. 144°. Similarly (IV) gives 2:11-diketo-9:18-dimethyl-1:2:9:10:11:18-hexahydrochrysene-b, m.p. 229°, the dihydrazone, m.p. 232—234° (decomp.), of which is converted into 9:18-dimethyl-1:2:9:10:11:18-hexahydrochrysene-b, dimorphous, m.p. 105—106°, and 101° (after resolidifying clears at 105°). H. G. M.

Synthesis and resolution of α -o-chlorobenzyl-ethylamine [β -o-chlorophenylisopropylamine].

I. B. JOHNS and J. M. BURCH (J. Amer. Chem. Soc., 1938, 60, 919—920).— $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{COCl}$ and ZnMeI give *o*-chlorobenzyl *Me* ketone, b.p. 125—130°/15 mm. (oxime, m.p. 120°), converted by $\text{HCO}\cdot\text{NH}_2$ and subsequent hydrolysis into β -o-chlorophenylisopropylamine, b.p. 75—80°/8 mm. (hydrochloride, m.p. 175—176°; *Bz* derivative, m.p. 135—136°), whence by *d*-tartaric acid is obtained the *d*-base, b.p. 75—77°/6 mm.; $[\alpha]_D^{25} +13.8^\circ$, $+11.4^\circ$ in MeOH , $+12.7^\circ$ in hexane (*d*-tartrate, m.p. 175°, $[\alpha]_D^{25} +21.1^\circ$ in H_2O ; hydrochloride, m.p. 175—176°, $[\alpha]_D^{25} +9^\circ$ in H_2O , $+4.1^\circ$ in MeOH ; *Bz* derivative, m.p. 166°, $[\alpha]_D^{25} +97.6^\circ$ in EtOH), which has the same configuration as *d*- $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{NH}_2$, since it is converted thereinto by $\text{H}_2\text{-Pd}$ in AcOH-EtOH . R. S. C.

Reduction of 2:4:6-trinitro-*m*-xylene. S. S. VORIS and P. E. SPOERRI (J. Amer. Chem. Soc., 1938, 60, 935—936).—Published statements about reduction of 1:3:2:4:6- $\text{C}_6\text{HMe}_2(\text{NO}_2)_3$ are confirmed. In addition, an excess of NH_4HS , best in dioxan, gives 71% of 2:4:1:3:6- $(\text{NO}_2)_2\text{C}_6\text{HMe}_2\cdot\text{NH}_2$ (I), m.p. 191° (hydrochloride; *Ac* derivative, m.p. 175°); TiCl_3 (equiv. to 1 NO_2) gives 3% of (I) and 51% of 2:1:3:4:6- $\text{NO}_2\cdot\text{C}_6\text{HMe}_2(\text{NH}_2)_2$, m.p. 213° (dihydrochloride); $\text{H}_2\text{-Raney Ni}$, promoted by PtCl_4 , in dioxan gives 99% of the triamine (dihydrochloride), reduction of the last NO_2 being relatively slow. R. S. C.

Water-soluble derivatives of *p*-aminobenzenesulphonamide [sulphanilamide]. I. H. G. KOLLOFF (J. Amer. Chem. Soc., 1938, 60, 950—951).— $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ and the appropriate amine in alkaline solution give *p*-acetamidobenzenesulphon-4'-, m.p. 253—254°, -3'-, m.p. 274—275°, and -2'-carboxyanilide, m.p. 240°, -di- β -hydroxyethylamide, m.p. 161—162°, and -anilide-4'-sulphonamide, m.p. 279—280°, *p*-acetamidobenzenesulphonylglycine, m.p. 237.5—238.5°, *Na* *p*-acetamidobenzenesulphonanilide-4'-sulphonate, hydrolysed by 4.9*N*- HCl to the corresponding *Ac*-free compounds, m.p. 202°, 196—197°, 315° (decomp.), 110—111°, — (hydrochloride, m.p. 224—225°, 150—151°, and —, respectively. $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ and $\text{NO}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ in warm EtOH give *p*-carbamidobenzenesulphonamide, m.p. 208—209°. R. S. C.

Sulphanilamides.—See B., 1938, 589.

Action of acid chlorides on anilides. C. A. FRIEDMANN and O. G. BACKEBERG (J.C.S., 1938, 469—470).— $\text{HCO}\cdot\text{NHPh}$ and AcCl at 100° yield diphenylformamidine (I) and a little NHAcPh , whilst with EtCOCl and BzCl , less of (I) and more of the anilide are formed. NHAcPh and AcCl yield a little diphenylacetamidine, which is also formed using $(\text{-CH}_2\cdot\text{COCl})_2$ (II), EtCOCl , or BzCl , the last two also yielding some propionanilide (III) and NHBzPh , respectively. With AcCl , EtCOCl , or BzCl , (III) yields only traces of basic substance. NHBzPh with AcCl yields small amounts of diphenylbenzamidine (IV), NBzAcPh , and BzCl , whilst EtCOCl affords (III) and BzCl , and (II) yields BzCl and (IV). J. D. R.

Symmetrical acylarylcarbamides. E. N. ABRAHART (J.C.S., 1938, 424—426).— $\text{NHBz}\cdot\text{CO}\cdot\text{NH}_2$

(I) and $\text{o-C}_6\text{H}_4\text{Cl-NH}_2$ at $175^\circ/2$ hr. yield *N*-benzoyl-*N'*-*o*-chlorophenylcarbamide, m.p. 212° ; from (I) and the appropriate amine are similarly formed *N*-benzoyl-*N'*-phenyl- [which with NH_2Ph at 220° yields NH_2Bz and $\text{CO}(\text{NHPh})_2$], -*o*-tolyl-, and -*p*-chlorophenylcarbamide. NHPhEt does not react with (I). $\text{p-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO-NH}\cdot\text{CO-NH}_2$ with the appropriate NH_2Ar at 165° yields *N*-*p*-nitrobenzoyl-*N'*-phenyl-, m.p. 232° , -*o*-tolyl-, m.p. 219° , and -*p*-tolyl-carbamide, m.p. 244° , also prepared from $\text{NH}_2\cdot\text{CO-NHAr}$ and $\text{p-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ in $\text{C}_5\text{H}_5\text{N}$. $3:2\text{-OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{COCl}$ (II) with $\text{NHPh}\cdot\text{CO-NH}_2$ in C_6H_6 yields *N*-3-hydroxy-2-naphthoyl-*N'*-phenylcarbamide (III), m.p. $303\text{--}305^\circ$ (decomp.; shrinks $275\text{--}280^\circ$), and a resin (which with KOH yields $3:2\text{-OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ and with NH_2Ph , $3:2\text{-OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO-NHPh}$). By the same method are prepared *N*-3-hydroxy-2-naphthoyl-*N'*-*o*-tolyl-, darkens and sinters at 310° , -*p*-tolyl-, m.p. $\sim 307^\circ$ (decomp.; blackens and shrinks 290°), -*o*-anisyl-, darkens and sinters 270° , -*p*-anisyl-, m.p. 240° (sudden heating; chars on slow heating), and -*p*-chlorophenylcarbamide, m.p. 240° (decomp.). With $\text{CO}(\text{NH}_2)_2$, (II) in C_6H_6 gives 3-hydroxy-2-naphthoylcarbamide, chars $270\text{--}275^\circ$, which with NH_2Ph (1 mol.) at $170\text{--}180^\circ/3$ hr. yields 2:4-diketo-3:4-dihydro- $\beta\beta$ -1:3-naphthoxazine, but with NH_2Ph in excess (1 hr.) yields (III).

J. D. R.

Congo-red [laboratory] synthesis. E. R. KLINE (J. Chem. Educ., 1938, 15, 129—131).—Details are given, using C_6H_6 and C_{10}H_8 as starting materials.

L. S. T.

Hydrazones from thiocyanophenylhydrazine. Z. HORII (J. Pharm. Soc. Japan, 1936, 56, 53—57; cf. A., 1937, II, 411).—*p*-Thiocyanophenylhydrazones of the following were prepared: COMe_2 , m.p. $128\text{--}129^\circ$; COEt_2 , m.p. $72\text{--}73^\circ$; COMeEt , m.p. $105\text{--}106^\circ$; COMePr , m.p. $94\text{--}95^\circ$; COMePr^β , m.p. 97° ; COMeBu , m.p. $88\text{--}89^\circ$; COMeBu^β , m.p. $89\text{--}90^\circ$; COMeBu^γ , m.p. 88° ; $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_3$, m.p. $63\text{--}64\text{--}65^\circ$; Me amyl ketone, m.p. $83\text{--}84^\circ$; Me iso-amyl ketone, m.p. $64\text{--}65^\circ$; COPhMe , m.p. $109\text{--}110^\circ$; $\text{C}_6\text{H}_4\text{X}\cdot\text{COMe}$, X = *p*-Cl, m.p. $143\text{--}143\text{--}5^\circ$, *p*-Br, m.p. 157° , *p*-I, m.p. $169\text{--}170^\circ$, *p*-Me, m.p. 145° , *p*-OMe, m.p. $146\text{--}147^\circ$, *o*-OH, m.p. $157\text{--}158\text{--}5^\circ$, *o*-OMe, m.p. $111\text{--}112^\circ$, *p*-NH₂, m.p. $156\text{--}156\text{--}5^\circ$; acetopyrocatechol, m.p. $134\text{--}134\text{--}5^\circ$; resacetophenone, m.p. 193° ; resacetophenone Me₂ ether, m.p. $117\text{--}118\text{--}5^\circ$; gallacetophenone, m.p. $192\text{--}192\text{--}5^\circ$; gallacetophenone Me₃ ether, m.p. $113\text{--}114\text{--}5^\circ$; $1:2\text{-OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{COMe}$, m.p. $211\text{--}212^\circ$; $\text{COMe}\cdot\text{CH}\cdot\text{CHPh}$, m.p. $155\text{--}156^\circ$; furfurylideneacetone, m.p. $143\text{--}143\text{--}5^\circ$; anisylideneacetone, m.p. $160\text{--}162^\circ$; $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$, m.p. $190\text{--}192^\circ$; *o*-, m.p. 160° , *m*-, m.p. $125\text{--}125\text{--}5^\circ$, and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$, m.p. $149\text{--}150^\circ$; *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CHO}$, m.p. 127° ; $4:3:1\text{-OH}\cdot\text{C}_6\text{H}_3\cdot\text{Br}\cdot\text{CHO}$, m.p. $127\text{--}129^\circ$; $3:4:1\text{-NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CHO}$, m.p. $186\text{--}187^\circ$; $5:2:1\text{-NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CHO}$, m.p. $213\text{--}214^\circ$; vanillin acetate, m.p. $123\text{--}124^\circ$; carbomethoxy-, m.p. $121\text{--}121\text{--}5^\circ$, and carbethoxy-vanillin, m.p. $106\text{--}107\text{--}5^\circ$; furfuraldehyde, m.p. 124° ; methylfurfuraldehyde, m.p. 132° ; AcCO_2H , m.p. $191\text{--}191\text{--}5^\circ$; lævulic acid, m.p. $156\text{--}5^\circ$.

CH. ABS. (c)

Configuration of isomeric diazocyanides and measurements of their rates of interconversion. R. J. W. LE FÈVRE and H. VINE (J.C.S., 1938, 431—438; cf. A., 1937, II, 376).—Measurement of the dipole moments of the isomeric pairs of 4-chloro- (I), 4-bromo- (II), 4-nitro- (III), 2-bromo- (IV), and 2:4:6-tribromo-benzenediazocyanide (V) (improved preps.) shows that the *cis*-isomerides are the less stable and are those primarily formed, and thus confirms the configurations allotted to the compounds by Hantzsch. The spontaneous isomerisation in C_6H_6 , followed by measurements of dielectric constant, shows that the change *cis* to *trans* is a unimol. reaction, and the relative rates of isomerisation are (I) and (II) > (III) and (IV) > (V).

J. D. R.

Structure of diazoamino-derivatives. (MLLE.) A. WOHL (Bull. Soc. chim., 1938, [v], 5, 460—468).—The absorption spectra of $\text{NPh}\cdot\text{N}\cdot\text{NMeR}$ and $\text{NR}\cdot\text{N}\cdot\text{NPhMe}$ ($\text{R} = \text{p-C}_6\text{H}_4\cdot\text{OMe}$ or C_{10}H_7) differ slightly. Spectra cannot decide between alternative formulæ for diazoamino-compounds in which the Me above is replaced by H. β -Naphthylidiazamino-benzenè, m.p. 150° , and *N*-methyl-*p*-anisylidiazamino-benzenes, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{NPhMe}$, m.p. 57° , and $\text{NPh}\cdot\text{N}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, m.p. 47° , are prepared. $\beta\text{-C}_{10}\text{H}_7\cdot\text{N}\cdot\text{N}\cdot\text{NPhMe}$, MeI, and KOH-EtOH give the triazine, $\text{NPh}\cdot\text{N}\cdot\text{NMe}\cdot\text{C}_{10}\text{H}_7$, m.p. $71\text{--}72^\circ$; the isomeric triazine, $\text{C}_{10}\text{H}_7\cdot\text{N}\cdot\text{N}\cdot\text{NPhMe}$, m.p. $97\text{--}98^\circ$, is obtained from $\beta\text{-C}_{10}\text{H}_7\cdot\text{N}_2\text{Cl}$ and NHPhMe .

R. S. C.

Exchange of hydrogen atoms between nitrophenols and water.—See A., 1938, 1, 315.

Manufacture of *o*-aminophenols.—See B., 1938, 487.

Derivatives of picramic acid. Their rearrangements. I. A. PEARL and W. M. DEHN (J. Amer. Chem. Soc., 1938, 60, 925—927).—With Ac_2O and a drop of H_2SO_4 at 100° picramic acid (I) gives the *N*-Ac derivative (II), new m.p. $204\text{--}205^\circ$ (obtained quantitatively by AcCl in hot C_6H_6 or from the NH_4 salt and warm Ac_2O), and 4:6-dinitro-1-methylbenzoxazole (III), m.p. 193° , considered by Schiff (A., 1886, 612) to be (IV) (below) and converted into (II) by HNO_3 , H_2SO_4 , or hot dil. alkali. If heated in Ac_2O containing a drop of H_2SO_4 and then kept therein at room temp. overnight, (I) gives (II) and the *O*-acetate (IV), m.p. $160\text{--}161^\circ$, hydrolysed by hot 5% NaOH , but rearranged into (II) by hot 0.2*N*- NaOH and converted [as is (II)] into (III) by hot Ac_2O . With BzCl or Bz_2O in hot C_6H_6 (I) gives the *N*-Bz derivative, m.p. $226\text{--}227^\circ$, converted by Ac_2O and a drop of H_2SO_4 at 100° into a mixture of 4:6-dinitro-2-benzamidophenyl acetate, m.p. $170\text{--}171^\circ$ [converted into (II) by dil. alkali], and 4:6-dinitro-1-phenylbenzoxazole, m.p. $220\text{--}221^\circ$. With hot ClCO_2Et (I) gives a 90—95% yield of the phenylurethane, m.p. $152\text{--}153^\circ$. The *N*-chloroacetyl, m.p. 150° , *N*-dichloroacetyl, m.p. $118\text{--}119^\circ$, and *N*- PhSO_2 , m.p. $202\text{--}203^\circ$ (acetate, m.p. $178\text{--}179^\circ$), derivatives of (I), 3:5-dinitro-2-hydroxy-*s*-diphenylthiocarbamide, m.p. $247\text{--}248^\circ$, and 4:6-dinitro-2-acetamidophenyl benzoate, m.p. $119\text{--}120\text{--}5^\circ$, are also prepared.

R. S. C.

Derivatives of higher ethers of pyrocatechol. G. K. HUGHES and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 103—111).—Pyrocatechol Bu^a_2 ether (I) and HNO_3 (*d* 1.42) in AcOH give the 4- NO_2 - (II), m.p. 56°, nitrated further to the 4:5-(NO_2) $_2$ -, m.p. 124°, -derivative (whence the 4-nitro-5-piperidino-compound, m.p. 51°), which with Zn in EtOH-HCl followed by phenanthraquinone (in aq. $NaHSO_3$ - $NaOAc$) yields 2:3-di-*n*-butoxyphenanthra-phenazine, m.p. 190°. (II) and aq. EtOH- Na_2S give 4-aminopyrocatechol Bu^a_2 ether (III), b.p. 157—158°/1.5 mm. [hydrochloride, m.p. 173°; picrate, m.p. 159°; 5- NO_2 -derivative, m.p. 108°; Ac derivative, m.p. 97° (5- NO_2 -, m.p. 85°, and 5-Br-, m.p. 87°, -derivatives)].

(I) and Br-AcOH afford 4-bromopyrocatechol Bu^a_2 ether, b.p. 195—197°/22 mm. [HNO_3 (*d* 1.42) in AcOH yields its 5- NO_2 -derivative, m.p. 62°], and the 4:5-Br $_2$ -, b.p. 206—208°/23 mm., derivative. (I) (in 70% H_2SO_4) with aq. CH_2O gives 2:3:6:7-tetra-*n*-butoxy-9:10-dihydroanthracene, m.p. 91°, partly debutylated with boiling 40% HNO_3 . *o*- $C_6H_4(OH)_2$ and *n*- $C_5H_{11}Cl$ in aq. EtOH-KOH give the di-*n*-amyl ether (IV), b.p. 174—176°/21 mm. [4- NO_2 -, m.p. 49°, and 4:5-(NO_2) $_2$ -, m.p. 117°, -derivatives]. β -(3:4-Di-*n*-butoxyanilino)propenyl Me ketone, b.p. 206—207°/1.5 mm. [from (III) and CH_2Ac_2], and conc. H_2SO_4 at <10°, yield 6:7-di-*n*-butoxy-2:4-dimethyl-quinoline, m.p. 49°, and some 6(or 7)-hydroxy-7(or 6)-butoxy-derivative, m.p. 180°. (I) and (IV) are dealkylated by $ClSO_3H$ and conc. H_2SO_4 . A. T. P.

Ethers of dihydric phenols.—See B., 1938, 486.

Nitro- and amino-derivatives of acylamido-quinol diaryl ethers and azo-dyes derived therefrom.—See B., 1938, 486.

New bismuth iodide derivative of "Aristol." W. POPLAWSKI (Arch. Chem. Farm., 1937, 3, 234—237).—Aristol [3:3'-di-iodo-4:4'-dihydroxy-2:2'-dimethyl-5:5'-dipropyldiphenyl (= RH_2)] and BiOI or BiI $_3$ yield the salt $[R_2BiI]_2$, insol. in H_2O and org. solvents. R. T.

Molecular structure in relation to cestrogenic activity. Compounds without a phenanthrene nucleus. E. C. DODDS and W. LAWSON (Proc. Roy. Soc., 1938, 125, B, 222—232).—Investigation of numerous compounds [e.g., 7:8-dihydroxyacenaphthenes; $CAr_3\cdot OH$; OH-derivatives of CH_2Ph_2 , $COPh_2$, $CHPh_3$, Ph_3 , $(-CH_2Ph)_2$, $CH_2(CH_2Ph)_2$, Ph_2O , and $NHPh_2$; $C_6H_4R\cdot OH$; hydrocarbons] shows that cestrogenic activity is not dependent on the phenanthrene ring. 4:4'-Dihydroxydiphenyl-alkanes and -alkylenes generally show activity; this varies with the length of, and the position of substituents attached to, the C chain, and also with the position of double linkings. Substituents in the aromatic nucleus other than OH generally lessen activity. *p*- $C_6H_4Pr^a\cdot OH$ is the only *p*-*n*-alkylphenol of the 9 tested to show activity; *p*- $OH\cdot C_6H_4\cdot CH\cdot CHMe$ (anol) is also active and can polymerise to highly active substances, but *p*- $OH\cdot C_6H_4\cdot CH_2\cdot CH\cdot CH_2$ is inactive. The following show varying degrees of activity (marked when designated *): 7:8-dihydroxy-7:8-di- α -naphthyl-acenaphthene* (I), m.p. 142° (from α - $C_{10}H_7\cdot MgBr$ and acenaphthenequinone); 7:7-di- α -naphthylacenaphth-

enone, m.p. 289° [from (I) and conc. HCl in boiling AcOH]; diphenyl- α -naphthylcarbinol (β -isomeride inactive); α -naphthyl-benzoin and -hydrobenzoin; 3:3'- and 4:4'-dihydroxydiphenylmethane; $\beta\beta$ -di-*p*-hydroxyphenyl-propane, -butane, and -pentane; $\gamma\gamma$ -di-*p*-hydroxyphenylpentane; $\alpha\alpha$ -di-*p*-hydroxyphenylheptane; α -phenyl- α -di-*p*-hydroxyphenyl-ethane; $\beta\beta$ -di-(4-hydroxy-3-methylphenyl)-propane and -butane; 4:4'-dihydroxytriphenylmethane; 1:1-di-*p*-hydroxyphenyl- and -di-(4-hydroxy-3-methylphenyl)-cyclohexane; 4:4'-di-, 2:3:4:4'-tetra-, and 2:3:4:3':4':5'-hexa-hydroxybenzophenone; *p*- $OH\cdot C_6H_4\cdot CHPh_2$; 2:4-dihydroxytriphenylacetic acid lactone; di- α -naphthyl-*p*-hydroxyphenylmethane*; 4:4'-dihydroxydiphenyl (its 3:3'-Me $_2$ derivative shows very slight activity); (*p*- $OH\cdot C_6H_4\cdot CH_2$) $_2$; phloridzin; phloretin; $\alpha\gamma$ -di-*p*-hydroxyphenylpropane; 2:4:6:4'-tetrahydroxy- $\alpha\gamma$ -diphenylpropane (+ H_2O), m.p. 158—159° (obtained by Clemmensen reduction of phloretin); $\alpha\epsilon$ -di-*p*-hydroxyphenylpentane; *p*- $OH\cdot C_6H_4\cdot OPh$; (*p*- $OH\cdot C_6H_4$) $_2O$; *p*-tert.-amyl- and *p*-cyclohexyl-phenol; *p*- $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH$; stilbene*, which is less active than $CHPh\cdot CPh_2$ * ($CPh_2\cdot CPh_2$ is inactive); *p*-hydroxy*- and 4:4'-dihydroxy-stilbene*; 4:4'-dihydroxytolane* (tolane is inactive); $\alpha\delta$ -diphenyl-butadiene*.

1:8-Di- α -naphthoynaphthalene, m.p. 227—228°, is obtained by oxidation (CrO_3 , AcOH) of (I). *p*-cyclopentylphenol is conveniently prepared from PhOH, cyclopentyl bromide, and $ZnCl_2$ (method: Bartlett and Garland, A., 1927, 968). H. B.

Polyhydroxytriphenylmethanes.—See B., 1938, 487.

Phenyl trifluoromethyl sulphides and sulphones.—See B., 1938, 486.

Esters of thio-acids. II. Derivatives of esters of thio-acids of arsenic and antimony and attempted preparation of the "ortho" thio-esters of these elements. R. KLEMENT and A. MAY (Ber., 1938, 71, [B], 890—894; cf. A., 1935, 1390).— $AsCl_3$ and *p*- $NHAc\cdot C_6H_4\cdot SH$ in C_6H_6 afford tri-*p*-acetamidophenyl thioarsenite (I), m.p. 108—111°; tri-*p*-acetamidophenyl thioantimonite (II), m.p. 165—168° (decomp.), and tri-*o*-carboxyphenyl thioarsenite (III), m.p. 208—210°, are obtained similarly. (I) and (III) are highly toxic. (II) resembles tartar emetic but is less poisonous. Attempts to obtain compounds of As^V or Sb^V by the action of halogen on (*p*- $C_6H_4Me\cdot S$) $_3As(Sb)$ gave (*p*- $C_6H_4Me\cdot S$) $_2$ and $AsCl_3$ or $SbCl_3$. $SbCl_5$ and *p*- $C_6H_4Me\cdot SNa$ (5 mols.) yield (*p*- $C_6H_4Me\cdot S$) $_2$ and $Sb(S\cdot C_6H_4Me\cdot p)_3$. The prep. of "ortho-" thio-acids of P, As, or Sb appears impossible. $SbCl_3$ and *o*- $SH\cdot C_6H_4\cdot CO_2H$ in anhyd. C_6H_6 yield the compounds, $SbCl(S\cdot C_6H_4\cdot CO_2H)_2$, m.p. 84—86°, and $SbCl_2(S\cdot C_6H_4\cdot CO_2H)_2$, m.p. 117—120°. H. W.

Sulphonation by sulphites. II. Simultaneous oxidation of β -naphthol and sodium sulphite. S. V. BOGDANOV and V. A. IVANOVA (J. Gen. Chem. Russ., 1937, 7, 2884—2894).—The yield of 2:1- $OH\cdot C_{10}H_6\cdot SO_3H$ obtained from β - $C_{10}H_7\cdot OH$ (I), aq. Na_2SO_3 , and CuO is not significantly affected by raising the temp. from 100° to 150°, or by varying the

relative concns. of the substrates, but rises abruptly as the ratio $C_{10}H_7 \cdot ONa : (I)$ exceeds 3 : 1, and attains 92% when the alkalinity corresponds with 100% Na salt; the yield of by-products [chiefly dinaphthol (II)] falls correspondingly. With MnO_2 in place of CuO the abs. yield is smaller, but increases more rapidly with rising alkalinity; only small amounts of (II) are formed. The reaction ceases before completion in both cases, this being more marked for MnO_2 than for CuO . (I) and CuO alone yield (II), the yield of which falls with rising alkalinity. Aq. Na_2SO_3 and CuO or MnO_2 at 130° yield chiefly Na_2SO_4 . Oxidation of Na_2SO_3 by atm. O_2 is greatly retarded in presence of (I). R. T.

Molecular rearrangement of (—)-phenylmethylcarbonyl *dl*-*p*-toluenesulphinate. C. L. ARCUS, M. P. BALFE, and J. KENYON (J.C.S., 1938, 485—493; cf. A., 1930, 1177).—The mol. rearrangement of (—)- and *dl*-phenylmethylcarbonyl *dl*-*p*-toluenesulphinate (I) to *dl*-*p*-tolyl- α -phenylethylsulphone (II) is studied. In the homogeneous state, (II) and a little styrene are formed from (I); in Et_2O -HCl (saturated), a little di-*p*-tolyl disulphoxide (III) and $CHPhMeCl$ are produced, but in Et_2O with 0.7% HCl, 0.1% NH_3 , or K_2CO_3 , (I) is unchanged. In C_6H_6 at room temp. (II) is formed in 21 days, but at 80° a little (III) is produced. No rearrangement takes place in $COMe_2$ at 56° or in C_5H_5N or $MeCN$ at room temp., but in $MeCN$ at 80° , (III) is formed whilst in $PhNO_2$, (II) is produced. In HCO_2H , (II) is formed together with *dl*-phenylmethylcarbonyl formate, b.p. $88-88.5^\circ/16$ mm., and (in presence of HCO_2Na) *p*- $C_6H_4MeSO_2H$. In HCO_2H with *p*- $C_6H_4MeSO_2Na$, both (II) and (III) are formed. (—)-Phenylmethylcarbonyl *dl*-*p*-toluenesulphinate, in the homogeneous state and in HCO_2H , yields (II); in HCO_2H with HCO_2Na , (—)+*dl*-phenylmethylcarbonyl formate and (—)+*dl*-*p*-tolyl- α -phenylethylsulphone (IV), $[\alpha]_{D_{40}}^{18} -65.6^\circ$ in $CHCl_3$, are formed, whilst with HCO_2H -*p*- $C_6H_4MeSO_2Na$, (II) and (IV), $[\alpha]_{D_{40}}^{23} -0.47^\circ$ (*l*, 0.236), are produced. The mechanism of the rearrangement is suggested (cf. *loc. cit.*) as : (a) (major reaction; ionic, with racemisation) the sulphinate is solvated to "active sulphinate", which undergoes reversible ionisation and irreversible racemisation to solvated ions, which recombine irreversibly to yield sulphone, and (b) (minor reaction; intramol. with retention of configuration) direct rearrangement to sulphone. This is supported by the observed rapid mutarotation of the (—)-ester in HCO_2H (which can only be ascribed to solvation), and the retention of activity in $MeCN$, which are parallel with the rapid transformation into sulphone in HCO_2H and the stability in $MeCN$. J. D. R.

Catalytic properties of rhenium. VII. Dehydrogenation of cyclohexanol over rhenium. E. V. TUR, S. B. ANISIMOV, and M. S. PLATONOV (J. Gen. Chem. Russ., 1937, 7, 2895—2898).—*Cyclo*-Hexanol yields chiefly *cyclo*hexanone, with traces of $PhOH$, C_6H_6 , and *cyclo*hexene, when passed over disperse Re at $350-400^\circ$. The chief product in presence of ReS_2 is $PhOH$. R. T.

Hydroxymethyl peroxides. I. Tetrahydro-naphthyl hydroxymethyl peroxide. K. I. IVA-

NOV, V. K. SAVINOVA, and E. G. MICHAILOVA (J. Gen. Chem. Russ., 1938, 8, 51—55).—1 : 2 : 3 : 4-Tetrahydro- β -naphthyl H peroxide in C_6H_6 and CH_2O (120 hr. at room temp.) yield 1 : 2 : 3 : 4-tetrahydro- β -naphthyl hydroxymethyl peroxide, m.p. 46.5° , which is decomposed by aq. $NaOH$, with liberation of H_2 . R. T.

Semi-hydrobenzoin change in the dehydration of phenylmethylvinyl glycol and the isomerisation of the corresponding epoxide. Y. DEUX (Compt. rend., 1938, 206, 1017—1019; A., 1937, II, 415).—The chlorohydrin of α -phenyl- β -methyl- Δ^{γ} -butadiene with KOH affords $\alpha\beta$ -oxido- α -phenyl- β -methyl- Δ^{γ} -butene (I), b.p. $80-83^\circ/6$ mm., which at $250-280^\circ/6$ mm. (on kieselguhr) or with $MgBr_2 \cdot Et_2O$ gives α -phenyl- α -methyl- Δ^{β} -butenaldehyde (II), b.p. $105^\circ/16$ mm. (oxime, m.p. $100-101^\circ$), reduced to β -phenyl- β -methylbutyl alcohol (*p*-nitrobenzoate, m.p. 64°), which when dehydrogenated (Cu) gives α -phenyl- α -methylbutaldehyde (cf. A., 1932, 392). (I) with 0.05N-HCl affords α -phenyl- β -methyl- Δ^{γ} -butene- $\alpha\beta$ -diol (*di*-*p*-nitrobenzoate, m.p. $97-98^\circ$), which when distilled in a vac. affords (II). J. L. D.

cis and trans-1 : 2-, 1 : 3-, and 1 : 4-dimethylcyclohexanols: dehydration with formic acid. G. CHURDOGLU (Bull. Soc. chim. Belg., 1938, 47, 241—259; cf. A., 1936, 201).—1 : 2-Dimethyl- (*cis*-, m.p. 23.2° , b.p. $82.8-82.9^\circ/25$ mm.; *trans*-, m.p. 13.2° , b.p. $74^\circ/25$ mm.), 1 : 3-dimethyl- (*cis*-, m.p. 27.5° , b.p. $84^\circ/25$ mm.; *trans*-, m.p. 14.5° , b.p. $77.5-77.6^\circ/25$ mm.), and 1 : 4-dimethyl- (*cis*-, m.p. 24° , b.p. $83.7-83.8^\circ/25$ mm.; *trans*-, m.p. 72.5° , b.p. $75.9-76.1^\circ/25$ mm.)-cyclohexanol, prepared from $MgMeBr$ and the corresponding 2-methyl-, m.p. -14° , b.p. $165.08^\circ/760$ mm. (semicarbazone, decomp. 197°), 3-methyl-, m.p. -73.5° , b.p. $169.58^\circ/760$ mm. (semicarbazone, decomp. 191.4°), and 4-methyl-, m.p. -40.6° , b.p. $171.25^\circ/760$ mm. (semicarbazone, decomp. 203.5°), -cyclohexanone, are converted (the 1 : 2-derivative most readily) by HCO_2H into 1 : 2-, b.p. $135.5-137.7^\circ/760$ mm., 1 : 3-, b.p. $128-128.4^\circ/760$ mm., and 1 : 4-, m.p. -59.4° , b.p. $128.7^\circ/760$ mm., -dimethyl- Δ^1 -cyclohexene, each respective hexene being identical, as shown by physical consts., whether obtained from the *cis*- or the more volatile *trans*-isomeride. The orientation of each pair of stereoisomeric carbinols is determined by the relative speeds of dehydration, being more rapid when H and OH are in the *trans*-position; this is in agreement with von Auwers' rule. Other physical consts., and details of experiments on dehydration velocities, are recorded. A. T. P.

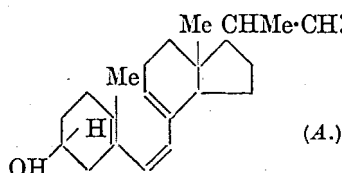
Methylation of triphenylcarbinol. H. H. HATT (J.C.S., 1938, 483—484).—With $MeOH$, CPh_3OH forms an additive compound, $CPh_3OH \cdot MeOH$, but is not methylated in absence of HCl. In presence of HCl (0.0001—1.0M), the dimorphous CPh_3OMe , m.p. $82.5-83^\circ$ (labile) and $96-96.5^\circ$ (stable), is formed. J. D. R.

Production of an antirachitic provitamin from cholesterol. N. A. MILAS and R. HEGGIE (J. Amer. Chem. Soc., 1938, 60, 984—985).—Cholesteryl acetate is shown spectroscopically to be converted into 7-dehydrocholesterol in small amounts by methylene-

blue or *p*-benzoquinone (I) + Pd in C_6H_6 in light, by chloranil or (I) + Pd at 120–130°, by succinodihydrogenase, and in better yield (20% in 6 hr.) by (I) at 120–130°. The last-mentioned treatment, followed by irradiation in Et_2O , gives an antirachiticall potent material.

R. S. C.

Constitution of tachysterol. W. GRUNDMANN (Z. physiol. Chem., 1938, 252, 151–154).—Ozonisation of tachysterol (I) does not afford CH_2O ; (I) does not contain the CH_2 group present in vitamin- D_2 (II). $(:C\cdot CO_2Me)_2$ and (I) readily give a non-cryst. adduct but tachysterol acetate yields the compound, $C_{36}H_{52}O_6$, m.p. 137°, which does not give a cryst. neutral or acid substance when treated with O_3 or $KMnO_4$. Results of previous attempts to determine the constitution of (I), and particularly the observation that the same products are not formed from it and from (II) by



oxidative degradation, suggest the constitution (A) for (I).

H. W.

Sugar-cane wax. II. Oxidation of sugar-cane sitosterol. T. MITUI (J. Agric. Chem. Soc. Japan, 1938, 14, 342–348; cf. A., 1937, III, 368).—Oxidation with CrO_3 gives *trans*-dehydroandrosterone, 3-hydroxy- Δ^5 -bismorcholenic acid, and 3-hydroxy- Δ^5 -ætiobilienic acid. As no 3-hydroxy- Δ^5 -norcholenic acid is formed, it is concluded the sitosterol contains the side-chain $\cdot CHMe\cdot CH_2\cdot CHMe\cdot CHMePr^{\beta}$.

J. N. A.

Derivatives of 3-epihydroxy-ætiocallocholane and -androstane.—See B., 1938, 589.

Esters of chaulmoogric acid. P. P. HERRERA and L. A. GUEVARA (Univ. Philippines Nat. and Appl. Sci. Bull., 1935, 4, 332–337; cf. A., 1930, 1579).—The following chaulmoogric esters were prepared by refluxing (3 days) the acid, alcohol, and $Et_2O\cdot HCl$: isoamyl, b.p. 225°/20 mm.; benzyl, b.p. 218°/10 mm.; phenylethylcarbinyl, b.p. 190°/10 mm.; phenylbutylcarbinyl, b.p. 193°/8 mm.

CH. ABS. (c)

cycloHexylideneacetic acid. C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1938, 494–496).—Attempts to resolve cyclohexylideneacetic acid (I) by way of the *brucine*, m.p. 55–57°, $[\alpha]_D^{25} \sim -30^\circ$ in $EtOH$, *quinine* (+2 H_2O), m.p. 98–104°, $[\alpha]_D^{25} \sim -137^\circ$ in $EtOH$, *strychnine*, m.p. 284–285°, *cinchonine*, and *cinchonidine* salts were fruitless. Attempts to resolve (I) and cyclohexanoneoxime with *Aspergillus niger*, *A. versicolor*, and a species of *Penicillium* were unsuccessful. *A. versicolor* attacks the *l*-form of lactic acid (as Na salt in a medium containing $NaNO_3$, KH_2PO_4 , KCl , $MgSO_4$, $FeSO_4$, and NH_4OAc) more rapidly than *A. niger* or *Penicillium*, and simultaneous destruction of the two antipodes is not so pronounced as with the other two.

J. D. R.

Conversion of phenylglycine into methyl-aniline.—See B., 1938, 483.

Arylamino propionic acids.—See B., 1938, 486.

Syntheses starting from hydrogen sulphite derivatives of esters of camphoceanaldehydic acid. J. VÈNE (Compt. rend., 1938, 206, 844–846).—The H sulphite compounds from Me and Et esters of camphoceanaldehydic acid (cf. A., 1932, 1037) with KCN afford Me, m.p. 127°, and Et 3-hydroxycyanomethyl-2 : 2 : 3-trimethylcyclopentane-1-carboxylate (I), m.p. 97°, which with 87% H_2SO_4 give β -carbamyl- β -campholide (II) but with 65–78% acid, β -cyano- β -campholide (III), m.p. 228°, is formed. (II) with HNO_2 affords β -carboxy- β -campholide, m.p. 213°, hydrolysed ($EtOH\cdot NaOH$) to 3-hydroxycarboxymethyl-2 : 2 : 3-trimethylcyclopentane-1-carboxylic acid, m.p. 198°. (I) with warm conc. KOH or (II) with 20% H_2SO_4 affords hydroxy-(3-carboxy-1 : 2 : 2-trimethylcyclopentyl)acetamide (IV), m.p. 143°, converted by dehydrating agents into (III) which itself is hydrolysed (hot $NaOH$) to (IV).

J. L. D.

Exchange of oxygen between benzil and water. Benzilic acid rearrangement. I. ROBERTS and H. C. UREY (J. Amer. Chem. Soc., 1938, 60, 880–882).—When Bz_2 (8.75 g.) is heated in $MeOH$ (20 c.c.) and H_2O (1.5 c.c.), containing 0.509% of $H_2^{18}O$, slight exchange of O occurs; much exchange occurs if 0.03 c.c. of 50% $NaOH$ is present. This confirms the chemical evidence that rearrangement to $OH\cdot CPh_2\cdot CO_2H$ occurs by rapid, reversible addition of $OH\cdot$ to give $COPh\cdot CPh(OH)\cdot O^-$, which slowly rearranges to $OH\cdot CPh_2\cdot CO_2^-$.

R. S. C.

Reaction of alkyl benzoates with sodium alkoxides. A. MAGNANI and S. M. McELVAIN (J. Amer. Chem. Soc., 1938, 60, 813–820).—Esters, $CH_2R\cdot OBz$, and $NaO\cdot CH_2R$ at 175–180° give reversibly $PhCHO$ and $R\cdot CHO$. Some or all of the following reactions may subsequently occur: (a) $R\cdot CHO + PhCHO \rightarrow R\cdot CO_2\cdot CH_2Ph$, (b) $2PhCHO \rightarrow CH_2Ph\cdot OBz$, (c) $2R\cdot CHO \rightarrow R\cdot CO_2\cdot CH_2R$, (d) $PhCHO + CH_2R'\cdot CHO \rightarrow [OH\cdot CHPh\cdot CHR'\cdot CHO] \rightarrow CO + OH\cdot CHPh\cdot CH_2R' \rightarrow CH_2Ph\cdot CO\cdot CH_2R'$, (e) $CH_2R'\cdot COPh + ROBz \rightarrow CHR'(COPh)_2$, (f) $CH_2R''\cdot CH_2\cdot OH + CH_2R'''\cdot CH_2\cdot ONa \rightarrow NaOH + CH_2R''\cdot CH_2\cdot CHR'''\cdot CH_2\cdot OH$. $BzOH$ is obtained by hydrolysis of the ester by H_2O liberated in the secondary reactions. Much $ROBz$ is recovered and some tar is formed. The max. yield (40%) of CH_2Bz_2 is obtained from 4 mols. of $EtOBz$ and 1 of $NaOEt$, and these proportions were used in all experiments. The following products were isolated in the mol. proportions stated: $R = H$: $BzOH$ 0.7, $MeOH$ 0.18, $CH_2Ph\cdot OBz$ (I) 0.01, and Me_2O 0.55 (formed by the reaction, $MeOBz + NaOMe \rightarrow NaOBz + Me_2O$); $R = Me$: $BzOH$ 0.55, $EtOH$ 1.8, CH_2Bz_2 0.4, (I) 0.15, CO 0.58, $COPhMe$ a trace; $R = Et$: $BzOH$ 0.9, Pr^aOH 1.57, (I) a trace, $CHPhEt\cdot OH$ 0.2, and its benzoate 0.31, CO 1.07, $CHMePr^a\cdot CH_2\cdot OH$ 0.04, and its benzoate 0.24, $COPhEt$ 0.06, and $CHPh\cdot CHMe$ a trace; $R = Pr^a$: $BzOH$ 0.85, Bu^aOH 1.27, (I) 0.04, CO 1.03, $CHPhPr^a\cdot OH$ 0.34, and its benzoate 0.41, $CHEtBu^a\cdot CH_2\cdot OH$ 0.1, and its benzoate 0.25, $COPhPr^a$ 0.07, and $CHPh\cdot CHEt$ a trace; $R = Pr^{\beta}$: $BzOH$ 1.02, $Bu^{\beta}OH$ 1.42, (I) 0.14, $Pr^{\beta}CO_2Bu^{\beta}$ 0.31, the benzoate 0.27 and isobutyrate 0.02 of $CHPhPr^{\beta}\cdot OH$ 0.19, $COPhPr^{\beta}$ 0.28, α -phenyl- Δ^2 -isobutene 0.03 (*dimide*, m.p. 143–146°), $Pr^{\beta}CHO$ and $Pr^{\beta}CO_2H$

traces; R = Bu': BzOH 0.86, CH₂Bu'·OH 0.83, (I) 0.14, Bu'CO₂·CH₂Ph 0.12, Bu'CO₂·CH₂Bu' 0.8, Bu'CHO 0.12, Bu'CO₂H 0.14, and a substance, C₁₈H₂₂O, m.p. 103—104°. When CH₂R is Pr^β, the products are: BzOH 0.6, Pr^βOH 1.8, CH₂Bz₂ 0.16, CPh·CH₂·COMe 0.08, (I) 0.11, COMe₂ trace. The following are incidentally described: β-methyl-n-amyl benzoate, b.p. 130—132°/9 mm., and α-naphthylurethane, m.p. 75—76°; α-phenylpropyl benzoate, b.p. 146—147°/3 mm.; β-ethyl-n-hexyl benzoate, b.p. 119—120°/2 mm., and α-naphthylurethane, m.p. 60—61°; p-phenylphenacyl α-methyl-n-valerate, m.p. 64—65°, and α-ethylhexoate, m.p. 53—54°; α-phenyl-n-butyl benzoate, b.p. 145—146°/2 mm., and α-naphthylurethane, m.p. 98—99°; α-phenylisobutyl α-naphthylurethane, m.p. 116—117°, and benzoate, b.p. 148—149°/3 mm. R. S. C.

New anæsthetic. E. GRYSZKIEWICZ-TROCHIMOWSKI and S. OTOLSKI (Arch. Chem. Farm., 1937, 3, 215—217).—NET₂[CH₂]₂NHET and OH·CH₂·CH₂Cl yield NN'N'-triethyl-N-β-hydroxyethylthylenediamine (I), b.p. 120—125°/10 mm., which with p-NO₂·C₆H₄·COCl in C₆H₆ gives the p-nitrobenzoyl ester of (I) (hydrochloride, m.p. 112°), reduced by Sn in HCl to the p-aminobenzoyl ester (mono-, m.p. 122—124°, and dihydrochloride, m.p. about 200°); the local anæsthetic action of this ester considerably exceeds that of novocaine. R. T.

Homologues of salol. Salicylates of the isomeric amylphenols and amylcresols. H. G. KOLLOFF and J. O. PAGE (J. Amer. Chem. Soc., 1938, 60, 948—949).—o-OH·C₆H₄·CO₂H, the appropriate phenol, and POCl₃ give 40—50% yields of o-, b.p. 155—157°/0.03 mm., and p-n-amylphenyl, b.p. 177—180°/2 mm., 3-, b.p. 141—145°/0.004 mm., and 5-n-amyl-o-, b.p. 140—142°/0.06 mm., and 4-n-amyl-m-tolyl, b.p. 156—160°/0.008 mm., 3-n-, b.p. 150—156°/0.05 mm., and 3-sec.-amyl-p-tolyl, b.p. 166—168°/0.018 mm., and 4-chloro-2-cyclohexylphenyl salicylate, m.p. 99.5—100°, which are hydrolysed at approx. the same rate as salol. 3-sec.-Amyl-p-cresol, b.p. 127—128°/13 mm. (3:5-dinitrobenzoate, m.p. 105°), is obtained in 25.2% yield from n-C₅H₁₁·OH, p-cresol, and ZnCl₂. R. S. C.

Trifluoromethylbenzoyl fluorides.—See B., 1938, 488.

Diaroyl peroxides.—See B., 1938, 488.

Benzoyl peroxide and benzylamine. S. GAMBARIAN, O. TSCHALTUIKJAN, and A. BABAJAN (Trans. VI Mendelev Cong. Chem. 1932, 1935, 2, Pt. I, 1001—1002; cf. de Paolini, A., 1931, 209, 638).—The reaction between Bz₂O₂ (I) and CH₂Ph·NH₂ (II) is: (I) + (II) = BzOH + CH₂Ph·NH·OBz (III); (III) + (II) = CH₂Ph·NHBz + CH₂Ph·NH·OH.

CH. ABS. (c)

Iodomethoxyphthalic acid from colchicine. R. GREWE (Ber., 1938, 71, [B], 907—911).—o-4-Xylenol Me ether is oxidised (KMnO₄, aq. NaOH) to 4-methoxyphthalic acid (yield about 60%), converted into 3-nitro-4-methoxyphthalic anhydride, which is reduced (Pd-sponge in AcOH) to 3-amino-4-methoxyphthalic anhydride, m.p. 182°; the corresponding acid, m.p. 152° (decomp.), gives 3-iodo-4-methoxy-

phthalic acid, m.p. 216° (decomp.) (anhydride, m.p. 206°). Benzenazo-o-4-xylenol is transformed into its Me ether, m.p. 67°, reduced (Na₂S₂O₄) to 5-amino-4-methoxy-o-xylene, b.p. 136°/15 mm., m.p. 91°. This yields 5-iodo-4-methoxy-o-xylene, b.p. 147°/15 mm., m.p. 37°, oxidised to 5-iodo-4-methoxyphthalic acid, m.p. 204° (decomp.) (anhydride, m.p. 168°), identical with the acid derived from colchicine (Windaus et al., A., 1915, i, 708). H. W.

cycloHexane group. R. MALACHOWSKI, J. J. WASOWSKA, and S. JÓZKIEWICZ [with J. ADAMCZKA and G. ZIMMERMAN-PASTERNAK] (Ber., 1938, 71, [B], 759—767).—No evidence of isomerism such as is required by Sachs' theory is obtained when cis- (I) and trans- (II) cyclohexane-1:4-dicarboxylic acids are converted into a series of derivatives; the latter can be isolated only in those two steric forms which are required by the plane model. cis-Hexahydroterephthalyl chloride (III), b.p. 97—97.5°/0.5 mm., is derived from (I) and SOCl₂ at 20° whilst prolonged boiling with SOCl₂ is required to convert (II) into trans-hexahydroterephthalyl chloride (IV), m.p. 67°. When heated at 190—200°, distilled under 9 mm., and then hydrolysed (III) gives 28% of (I) and 72% of (II) whereas (IV) yields 31% of (I) and 69% of (II). NH₃ transforms (III) into cis-hexahydroterephthaldiamide, m.p. 232° (corr.), isomerised when heated at a higher temp. to trans-hexahydroterephthaldiamide, m.p. 346° (decomp.), obtained also from (IV) and 25% NH₃. Treatment of the diamides with boiling SOCl₂ gives cis-1:4-dicyanocyclohexane (V), m.p. 65°, hydrolysed by 20% HCl to (I) and by 30% KOH to (II); the trans-dinitrile, m.p. 140° (corr.), is hydrolysed by acid or alkali to (II). Hydrogenation (PtO₂ in Ac₂O) of (V) gives the Ac₂ derivative, m.p. 150° (corr.), of cis-1:4-di(aminomethyl)cyclohexane, b.p. 113—115°/8 mm., m.p. -9° [dihydrochloride (VI), m.p. 350° (decomp.)]; platinichloride, m.p. 295° (decomp.); Bz₂ derivative, m.p. 219° (corr.). trans-1:4-Di(aminomethyl)cyclohexane (VII), b.p. 116—118°/10 mm., m.p. 27° [Ac₂ derivative, m.p. 230° (corr.)]; dihydrochloride, decomp. >380°; platinichloride, decomp. >300°; Bz₂ derivative, m.p. 253°, is described. Dry distillation of (VI) yields p-methylenecyclohexylmethylamine, b.p. 68—70°/10 mm. [very hygroscopic hydrochloride; platinichloride, m.p. 198° (decomp.); Bz derivative, m.p. 95°], exhaustively methylated to the compound, C₁₁H₂₂NI, m.p. 208—210° (corr.). Reduction (Bouveault-Blanc) of the isomeric Me₂ hexahydroterephthalates gives a mixture of cis-, b.p. 167°/10 mm., m.p. 43°, and trans-, b.p. 163—165°/10 mm., m.p. 67°, -1:4-di(hydroxymethyl)cyclohexane, separated from one another by crystallisation of the corresponding dibenzoates, m.p. 86° and 125°, respectively. The glycols are converted by HBr at 135—140° into cis-, non-cryst., and trans-, m.p. 55°, -1:4-di(bromomethyl)cyclohexane; the latter is converted by o-C₆H₄(CO)₂NK into the diphthalimido-derivative, m.p. 275° (corr.), hydrolysed to (VII). H. W.

Sodium [dihydronaphthyl]. II. Preparation and properties of dihydronaphthalenedicarboxylic acids. J. F. WALKER and N. D. SCOTT (J. Amer. Chem. Soc., 1938, 60, 951—955; cf. A., 1937, II, 55).—Passage of CO₂ into Na and C₁₀H₈ in Me₂O

or $(\text{CH}_2\text{OMe})_2$ at -70° to -80° , or at $>-70^\circ$ for dil. solutions, gives 45–50% of 1:4-dihydronaphthalene-1:4- (I), m.p. 229–230°, and 28–32% of 1:2-dihydronaphthalene-1:2-dicarboxylic acid (II), m.p. 185–190°, converted by $\text{K}_3\text{Fe}(\text{CN})_6\text{-KOH}$ into α - and β - $\text{C}_{10}\text{H}_7\text{CO}_2\text{H}$, respectively. By the above procedure only half the C_{10}H_8 is used, but all is used if the Na and CO_2 are added alternately. In $(\text{CH}_3\text{OEt})_2$ 62% of (II) is obtained. With Br-AcOH (I) gives 1:4- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$, but (II) gives (?) $\text{C}_{10}\text{H}_8\text{Br}_2(\text{CO}_2\text{H})_2$, m.p. 227° (decomp.). R. S. C.

Acids derived by oxidation of ovarian follicular hormones.—See B., 1938, 590.

Condensation and polymerisation of $\alpha\beta$ -unsaturated aldehydes and acids. II. Condensation of hexa- and tetra-hydrobenzaldehyde with acraldehyde. A. J. BERLIN and S. M. SCHERLIN (J. Gen. Chem. Russ., 1938, 8, 16–21).—1:2:3:6-Tetrahydrobenzaldehyde and $\text{CH}_2\text{CH=CHO}$ with quinol (SO_2 catalyst; 1 hr. at 105° , followed by 1 hr. at 120°) yield 1- β -formylethyl-1:2:3:6-tetrahydrobenzaldehyde, b.p. $140\text{--}142^\circ/14$ mm., oxidised (AgNO_3 in aq. NaOH) to 1- β -carboxyethyl-1:2:3:6-tetrahydrobenzoic acid, m.p. 161° . 1- β -Formylethylhexahydrobenzaldehyde, b.p. $120\text{--}121^\circ/7$ mm. (prepared as above), gives the lactone of 1- β -carboxyethylhexahydrobenzyl alcohol, b.p. $110\text{--}112^\circ/0.5$ mm., when heated with MeOH-KOMe , and yields 1- β -carboxyethylhexahydrobenzoic acid, m.p. $130\text{--}131^\circ$, when oxidised.

R. T.

α -Naphthaldehyde and its derivatives. H. W. COLES and (MISS) M. L. DODDS (J. Amer. Chem. Soc., 1938, 60, 853–854).—With 30% CH_2O and conc. HCl , followed by conc. H_2SO_4 , at 60° , C_{10}H_8 gives 67–70% yields of 1- $\text{C}_{10}\text{H}_7\text{CH}_2\text{Cl}$ (I), b.p. $291\text{--}292^\circ/760$ mm., $150^\circ/9$ mm. (changes fairly readily to a Cl-free polymeride, m.p. about 200°), and a substance, m.p. 125° . (I) with $(\text{CH}_2)_6\text{N}_4$ gives 59–60% of 1- $\text{C}_{10}\text{H}_7\text{CHO}$ (oxime, m.p. 98°); diphenylsemicarbazone, m.p. 197° ; semicarbazone, m.p. 219° ; thiosemicarbazone, m.p. 217° ; phenyl-, m.p. 82° , as-diphenyl-, m.p. 100.5° , β -naphthyl-, m.p. $174\text{--}175^\circ$, p -nitro-, m.p. 237° , 2:4-dinitro-, m.p. 254° , p -bromo-, m.p. $136\text{--}137^\circ$, and 2:5-dichloro-phenyl-hydrazone, m.p. 114° ; anil, m.p. 172° , and o -tolil, m.p. 172.5° . Di-(β -1-naphthylvinyl) ketone has m.p. 130° . M.p. are corr.

R. S. C.

Mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. IX. The *ortho*-effect in the reaction of phenacyl bromides with pyridine. J. W. BAKER (J.C.S., 1938, 445–448).— o -Methylacetophenone (semicarbazone, m.p. 206° ; lit., 203° , 192°) with Br yields o -methylphenacyl bromide, b.p. $113.5^\circ/1.7$ mm.; similarly, p -tert.-butylacetophenone [semicarbazone, m.p. $231\text{--}232^\circ$ (decomp.)] yields p -tert.-butylphenacyl bromide, b.p. $127^\circ/0.5$ mm. The kinetics of quaternary salt formation (in 0.025M solution in dry COMe_2) from $\text{C}_6\text{H}_5\text{N}$ and $\text{COPh-CH}_2\text{Br}$ (I), o - (II) and p -methyl- (III), 2:4-dimethyl- (IV), p -tert.-butyl- (V), o - (VI) and p -nitro- (VII), and 2:4:6-trimethyl-phenacyl bromide (VIII) show that the reaction is bimol. and is favoured by electron recession from the side-chain to the nucleus, the val.

of the velocity coeff. (k) following the order (VII) > (I) > (III) > (V) > (II) > (IV) > (VI) > (VIII). For (VIII), k was too small to be measured. The low val. of k for (II), (IV), and (VIII) is explained on the basis of the occurrence of resonance between the CO and o -Me group, and is supported by the fact that 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\text{COMe}$ and (VIII) do not react with semicarbazide acetate in EtOH [(IV) similarly yields ω -semicarbazido-2:4-dimethylacetophenone, m.p. $175\text{--}176^\circ$]. The retarding effect of o - NO_2 is ascribed to the electron-repelling effect of the negative O atoms acting directly (through the medium) on the side-chain, since chelation is unlikely. The following are described: o -nitro-, decomp. $\sim 260^\circ$, o -methyl-, m.p. 182° , and 2:4:6-trimethyl-phenacylpyridinium bromide, decomp. $\sim 280^\circ$. J. D. R.

Condensation of nitro- and amino-acetophenones with formaldehyde and secondary amines. C. MANNICH and M. DANNEHL (Arch. Pharm., 1938, 276, 206–211).— o - or m - $\text{NO}_2\text{-C}_6\text{H}_4\text{COMe}$, the hydrochloride of the *sec.* amine, and paraformaldehyde are heated in AcOH until the dark mixture has become homogeneous and miscible with H_2O . Thus are obtained the hydrochlorides of m -nitro- ω -dimethylamino-, m.p. 209° (decomp.) [corresponding phenylhydrazones, m.p. 76° , and its hydrochloride, m.p. 180° (decomp.)], ω -diethylamino-, m.p. 122° , ω -piperidino-, m.p. $171\text{--}172^\circ$, o -nitro- ω -dimethylamino-, m.p. 180° (decomp.), ω -diethylamino-, m.p. $146\text{--}147^\circ$, and ω -piperidino-, m.p. 183° (decomp.), -*propiophenone*. Addition of NaOH or Na_2CO_3 to an aq. solution of the salts causes an immediate strong odour of amine and a resin separates when the mixture is warmed. Normal reduction of NO_2 in slightly acid solution appears impossible. Resins result when condensations between o - or m - $\text{NH}_2\text{-C}_6\text{H}_4\text{COMe}$, o - $\text{NHAc-C}_6\text{H}_4\text{COMe}$, or o - $\text{NHBz-C}_6\text{H}_4\text{COMe}$, CH_2O , and NHMe_2HCl are attempted. m - $\text{NHAc-C}_6\text{H}_4\text{COMe}$ gives m -acetamido- ω -dimethylaminopropiophenone hydrochloride (I), m.p. 194.5° and m - $\text{NHBz-C}_6\text{H}_4\text{COMe}$ yields m -benzamido- ω -dimethylaminopropiophenone hydrochloride (II), m.p. 178° ; basification of these salts causes liberation of NHMe_2 . Reduction of (I) by Na-Hg in slightly acid solution yields m -acetamidophenyl- β -dimethylaminoethylcarbinol, m.p. 123° , which gives a benzoate hydrochloride, m.p. 185° , devoid of anaesthetising action. Boiling HCl converts (II) into m -amino- ω -dimethylaminopropiophenone (dihydrochloride, decomp. $>180^\circ$), reduced to m -aminophenyl- β -dimethylaminoethylcarbinol, m.p. 74° . The corresponding o -compounds could not be obtained in this manner. H. W.

Synthesis of compounds related to the antirachitic vitamins. Condensation of cyclohexylideneacetaldehyde with 4-hydroxycyclohexanone. J. B. ALDERSLEY and G. N. BURKHARDT (J.C.S., 1938, 545).—Ozonolysis of 1-allylcyclohexanol yields cyclohexylideneacetaldehyde (I) (semicarbazone, m.p. 205°) and cyclohexenylacetaldehyde (semicarbazone, m.p. 186°). 4-Acetoxy-cyclohexanone (semicarbazone, m.p. $182\text{--}183^\circ$) and (I) in aq. NaOH yield α -cyclohexylidene- β -(5-hydroxy-2-ketocyclohexylidene)ethane (phenylurethane, m.p. 180° ; 2:4-dinitrophenylhydrazones, m.p. $170\text{--}171^\circ$). J. D. R.

Stereochemistry of cyclanes. I. R. CORNUBERT. II. Stereoisomeric monobenzylidene derivatives. R. CORNUBERT, M. ANDRÉ, M. DE DEMO, R. JOLY, P. LOUIS, P. ROBINET, and A. STRÉBEL. **III. Stereoisomeric benzylidene-2-methylcyclopentanones and -hexanones.** R. CORNUBERT and P. LOUIS. **IV. Stereoisomeric benzylidene derivatives of 2-benzyl- and 2-isopropyl-cyclopentanones. Benzylidene derivatives of 2:2-dialkylcyclohexanones. Alteration of benzylidene derivatives.** R. CORNUBERT, M. ANDRÉ, M. DE DEMO, P. LOUIS, and A. STRÉBEL (Bull. Soc. chim., 1938, [v], 5, 509—512, 513—520, 520—534, 534—546; cf. A., 1932, 746 and preceding abstracts).—With the possible exception of 2:6-dibenzylcyclohexanone, the no. of isomeric cyclohexanone and -pentanone derivatives is in accord with a planar structure of the ring. 6-Benzylidene-2-methylcyclohexanone (I), m.p. 62—63° (semicarbazone, m.p. 212°; oxime, m.p. 147°), is converted by HCl in cyclohexanol into (or, if prepared in acid solution, is accompanied by) an isomeric form (II), b.p. 156—157°/7 mm. (semicarbazone, m.p. 183°; oxime, m.p. 107°; oximinooxime, m.p. 187°). (I) reacts more readily than does (II) with CO-reagents, Br, O₂, H₂ (Ni), and MgPhI, and is oxidised more readily by KMnO₄ to BzOH and α -methyladipic acid [obtained only from (I)]. With MgPhI (1 mol.) (I) gives 2-benzhydryl-6-methylcyclohexanone, m.p. 140—141°, but with 1.25 mols. gives also a stereoisomeride (III), m.p. 95—103°; with HCl-PhCHO both these products give three substances, C₂₇H₂₇OCl (? 6- β -chloro- $\alpha\alpha$ - β -triphenylethyl-2-methylcyclohexanone), m.p. 103—109°, 166—167°, and 166—167°, respectively, and in one experiment (III) gave also a small amount of a tetrahydropyrene derivative, C₃₄H₃₂O₂, m.p. 250—252°. Methylation of Et cyclopentanone-2-carboxylate by MeI gives also Et₂ α -methyladipate; the reaction is influenced by impurities (b.p. >44°) in the MeI. The decarboxylation of Et 2-methylcyclopentanone-2-carboxylate is modified. The solid form (IV) of 5-benzylidene-2-methylcyclopentanone yields the liquid form when heated at 280—290° or kept with HCl in cyclohexanol; Speranski's form of m.p. 124° was not obtained, but his method led to some 2- α -hydroxybenzyl-5-methylcyclopentanone (V), m.p. 160—161°, which with hot Ac₂O gives (IV) and (?) an isomeride, m.p. 166—168°, of (V). Partial hydrogenation (Co or Ni formate) of 2:6-dibenzylidenecyclopentanone gives a form (VI), m.p. 129—130°, and its trimeride (VII), m.p. 240°, of 2-benzyl-5-benzylidenecyclopentanone, (VI) being also obtained from 2-benzylcyclopentanone and PhCHO with NaOMe; use of HCl at -10° in this last condensation gives a form (VIII), b.p. 248—250°/18 mm., which is obtained from (VI) by HCl in cyclohexanol. (VII) is obtained from (VI) by irradiation (ultraviolet), or by keeping. (VI) gives a semicarbazone, m.p. 207—208°, and an oxime, m.p. 108—109°; it is oxidised to BzOH and hydrogenated to 2:6-dibenzylcyclopentanone (IX), m.p. 39°. (VIII) is reduced to (IX) [in one case, crude (VIII) gave the isomeride, m.p. 58°, of (IX)], gives a semicarbazone, m.p. 161°, and an oxime, m.p. 174°. (VII) resists hydrogenation and oxidation, and is stable to HCl. The solid form of 5-benzylidene-2-isopropylcyclopentanone (X) (semi-

carbazone, m.p. 206—207°) with HCl gives the liquid form (semicarbazone, m.p. 169—170°). 2:2-Dimethyl- and 2-methyl-2-isopropyl-cyclopentanone and 2-methyl-2-propylcyclohexanone give each only one benzylidene derivative; 6-benzylidene-2-methyl-2-propylcyclohexanone gives a semicarbazone, m.p. 183—184°, but the C₅-ring compounds give no semicarbazones. In air (or by irradiation) (I) gives an oxide, C₁₄H₁₆O₃, m.p. 122—123°. (IV) gives a similar oxide, m.p. 29—30°. 2-Benzyl-6-benzylidenecyclohexanone gradually acquires a higher and indefinite m.p., and 2-benzyl-6-benzylidene-2-propylcyclohexanone gives a liquid isomeride, but other similar substances are unchanged. Irradiation of (IV), (VIII), and (X) gives oxides, but the liquid isomeride of (X) is unaffected. 2-Benzyl-6-benzylidenecyclohexanone, m.p. 76°, prepared by NaOMe or HCl, gives, when irradiated, a (?) tetrameride, m.p. 224°. R. S. C.

Substituted tetrahydronaphthalenes. I. 1-Keto- and 1-hydroxy-2-p-dialkylaminobenzyl-tetrahydronaphthalenes. R. L. SHRINER and W. O. TEETERS (J. Amer. Chem. Soc., 1938, 66, 936—939).—Addition of 1-keto-1:2:3:4-tetrahydronaphthalene (I) to the appropriate dialkylamino-aldehyde in NaOH-EtOH-H₂O and heating at 100° gives the 2-p-di-methyl- (II), m.p. 155.5—156.5° (oxime, m.p. 207.5—208°), -ethyl-, m.p. 95—95.5°, and -n-propyl-aminobenzylidene derivatives, m.p. 123—123.5°, hydrogenated in warm EtOH in presence of PtO₂ only to 1-keto-2-p-di-methyl-, m.p. 112—112.5° (oxime, m.p. 166.5—167.5°), -ethyl-, m.p. 57.5—58°, and -n-propyl-aminobenzyl-1:2:3:4-tetrahydronaphthalene, m.p. 65.5—66°. Hydrogenation of (II) in warm EtOH in presence of Raney Ni gives 2-p-dimethylaminobenzyl-1:2:3:4-tetrahydro- α -naphthol, α - (III), m.p. 100—100.5° [hydrochloride, m.p. 175—176° (decomp.)], and β -form (IV), b.p. 195—198°/2 mm. (hygroscopic hydrochloride). PtO₂-hydrogenation of 2-p-dimethylaminobenzylidenecyclohexanone yields 2-p-dimethylaminobenzylcyclohexanol (V), b.p. 156—158°/3 mm. [hydrochloride, m.p. 194—195.5° (decomp.)], whilst p-NMe₂·C₆H₄·CH₂·CH₂·COPh at 3 atm. gives α -phenyl- γ -p-dimethylaminophenylpropyl alcohol (VI), b.p. 182—188°/3 mm. (oily hydrochloride), and the p-chlorobenzylidene derivative of (I) at 3 atm. gives 2-p-chlorobenzyl-1:2:3:4-tetrahydro- α -naphthol, α -, m.p. 124—124.5°, and β -form, m.p. 91—92°. M.p. are corr. The CO-amines are very irritant to the rabbit's eye, but not toxic to cats or analgesic in mineral oil to mice. The hydrochlorides of (IV), (V), and (VI) have local anæsthetic action on guinea-pig's skin and rabbit's eye, but that of (III) only on guinea-pig's skin; details are given. R. S. C.

Polyphenylation of $\alpha\alpha'$ -ditolyl derivatives. V. 4-Benzhydrylfluorenone. P. G. SERGEEV (J. Gen. Chem. Russ., 1938, 8, 3—6).—2-Benzhydryldiphenyl-2'-carboxylic acid in C₆H₆ is heated with PCl₅ until evolution of HCl ceases, and then with AlCl₃, to yield 4-benzhydrylfluorenone (I), m.p. 178—179°. 4-Fluorenylfluorenone, m.p. 218—219°, is obtained similarly from 2-fluorenyldiphenyl-2'-carboxylic acid. (I) and MgPhBr in Et₂O afford 9-phenyl-4-benzhydrylfluorenone, m.p. 167—168°, the bromide of which gives intensely coloured solutions when boiled with C₅H₅N. R. T.

Benzantrones. I. Mechanism of Bally's reaction. F. G. BADDAR and F. L. WARREN (J.C.S., 1938, 401—404; cf. A., 1937, II, 457).—The mechanism proposed by Bally and Scholl (A., 1911, i, 676) for the synthesis of *mesobenzanthrone* from glycerol, H_2SO_4 , and anthraquinone (I) is considered to be correct since (I) and α -ethylglycerol in aq. H_2SO_4 with Cu yield anthranol and 1'-ethylmesobenzanthrone (II), m.p. 106° , the constitution of which is proved as follows. $1\text{-C}_{10}\text{H}_7\text{Et}$ and 99% HNO_3 in AcOH yield 4-nitro-1-ethylnaphthalene, b.p. $164\text{--}165^\circ/3$ mm., reduced by $\text{SnCl}_2\text{-HCl}$ in EtOH to 4-ethyl- α -naphthylamine, b.p. $170^\circ/8$ mm. (Ac derivative, m.p. 151°), converted (diazo-method) into 4-iodo-1-ethylnaphthalene (III), b.p. $170^\circ/7$ mm. $o\text{-C}_6\text{H}_4\text{I}\cdot\text{CO}_2\text{Me}$ and (III) with Cu at 180° , followed by hydrolysis, yield $o\text{-4'-ethyl-1'-naphthylbenzoic acid}$, m.p. 176° , which is converted (Friedel-Crafts; hot 90% H_2SO_4) into (II) and 2'-ethyl-3:4-benzfluorenone, m.p. 139° . Similarly, $o\text{-1'-naphthylbenzoic acid}$ gives *mesobenzanthrone* and benzfluorenone (cf. A., 1918, i, 434).

J. D. R.

Polycyclic systems. I. Condensation of chrysene with succinic anhydride. H. BEYER (Ber., 1938, 71, [B], 915—922).—Addition of AlCl_3 to $(\text{-CH}_2\text{CO})_2\text{O}$ (I) and chrysene in C_6H_6 at $35\text{--}40^\circ$ gives $\beta\text{-2-chrysenoylpropionic acid}$ (II), m.p. $197\text{--}198^\circ$ (slight decomp.) [*Na salt*; *Me*, m.p. $135\text{--}136^\circ$, and *Et*, m.p. $105\text{--}106^\circ$ (clear at 107°), esters; *semicarbazone* (III), m.p. $237\text{--}239^\circ$ (decomp.)], in 50—55% yield. At room temp. the yield is about 30—35% whereas at $70\text{--}80^\circ$ more resinous matter is produced whereby the amount and purity of the acid are greatly depressed. Reduction (Clemmensen) of (II) affords

$\gamma\text{-2-chrysenylbutyric acid}$, m.p. $208\text{--}209^\circ$ (*Me ester*, m.p. $125\text{--}126^\circ$ becoming transparent at 127°), also derived (Wolff-Kishner) from (III). This is converted by the successive action of PCl_5 in C_6H_6 and AlCl_3 in PhNO_2 into 1'-keto-1':2':3':4'-tetrahydro-1:2-benzochrysene (A), m.p. $220\text{--}221^\circ$, which does not give a semicarbazone, oxime, or *p*-nitrophenylhydrazone; it is reduced (Clemmensen) to 1'-hydroxy-1':2':3':4'-tetrahydro-1:2-benzochrysene, m.p. $181\text{--}182^\circ$, which appears indifferent to Ac_2O . In PhNO_2 chrysene, (I), and AlCl_3 give (?) $\beta\text{-1-chrysenoylpropionic acid}$, m.p. $221\text{--}223^\circ$ (*Me ester*, m.p. $148\text{--}149^\circ$), reduced to $\gamma\text{-1-chrysenylbutyric acid}$, m.p. $213\text{--}214^\circ$ (*Me ester*, m.p. $100\text{--}101^\circ$).

H. W.

Synthesis of linear polynuclear aromatic compounds. C. MARSCHALK (Bull. Soc. chim., 1938, [v], 5, 306—309).—Condensation of $2:3\text{-C}_{10}\text{H}_6(\text{CO})_2\text{O}$ (I) with dihydroquinizarin (II) (trace of AlCl_3) (cf. A., 1936, 1256) gives a hydroxy-ketone probably of the *lin.*-hexacene series. Similar products are obtained from leuco-1:4-dihydroxynaphthacenequinone (III) and $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ or $o\text{-CHO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (condensation in presence of $\text{Na}_2\text{S}_2\text{O}_4$, cyclisation by NaCl-AlCl_3). (I) and (III) give a compound, probably derived from *lin.*-heptacene (IV). 1:4-Dihydroxyanthraquinone-2:3-dicarboxylic anhydride does not condense, but anthraquinone-2:3-dicarboxylic an-

hydride (V) and leucoquinizarin (trace of AlCl_3) give a derivative of (IV). From anthracene- and anthraquinone-dicarboxylic anhydrides and (III), products probably derived from *lin.*-octacene are obtained. Pyromellitic anhydride condenses (cf. A., 1911, i, 793) with (II) to a substance sol. in aq. Na_2CO_3 (unlike the above). Quinol and (V) give (AlCl_3) 6:7-phthaloylquinizarin (?). E. W. W.

Substances with female hormone effect. I. J. HOCH (Bull. Soc. chim., 1938, [v], 5, 264—276).—In part a more detailed account of work already reported (A., 1937, II, 423). 1-Keto-1:2:3:4-tetrahydrophenanthrene (*loc. cit.*), $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$, and Zn in C_6H_6 give *Et* $\alpha\text{-3:4-dihydro-1-phenanthrylpropionate}$, b.p. $207\text{--}210^\circ/1$ mm., the H_2 -derivative of which is hydrolysed and the acid cyclised by SnCl_4 to the 1-*Me* derivative, m.p. 138° (*oxime*, m.p. $150\text{--}151^\circ$), of 4:5-benzo-6:7:8:9-tetrahydroacene-naphthen-2-one (cf. *loc. cit.*) (which is now found to have about 1/60 the activity of folliculin). $\beta\text{-6-Methoxy-1:2:3:4-tetrahydro-1-naphthylethanol}$ (A., 1936, 990), new m.p. 58° (*phenylurethane*, m.p. 75°), in C_6H_6 gives (PBr_3) the corresponding bromide, new b.p. $195\text{--}196^\circ/15$ mm., which is converted (cf. A., 1936, 990) into $\gamma\text{-6-methoxy-1-naphthylbutyric acid}$, and thence (cf. A., 1936, 76) into 1-keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene (I). With $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and Zn-Hg (not Zn) in C_6H_6 (I) gives the *Et ester*, b.p. $235\text{--}240^\circ/2$ mm., of 7-methoxy-3:4-dihydro-, m.p. $170\text{--}172^\circ$ (decomp.), which is hydrogenated to 7-methoxy-1:2:3:4-tetrahydro-1-phenanthrylacetic acid, m.p. 188° (not yet cyclised). With $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$, (I) yields the *Et ester*, b.p. $220\text{--}235^\circ/2$ mm., of $\alpha\text{-7-methoxy-3:4-dihydro-}$, m.p. 180° (decomp.), which is hydrogenated to $\alpha\text{-7-methoxy-1:2:3:4-tetrahydro-1-phenanthrylpropionic acid}$, m.p. 172° (not yet cyclised).

E. W. W.

Transition from the androsterone to the progesterone series. A. BUTENANDT and J. SCHMIDT-THOMÉ (Naturwiss., 1938, 26, 253).—Dehydroandrosterone acetate with KCN-AcOH in EtOH yields the two isomerides, m.p. 195° and 203° , of 17-cyanoandrosterone-3:17-diol 3-acetate, the mixture of which, dehydrated with POCl_3 and $\text{C}_6\text{H}_5\text{N}$, yields 17-cyano-3-acetoxy- $\Delta^{5:16}$ -androstadiene, m.p. 210° , which, with MeMgI at Et_2O , yields $\Delta^{5:16}$ -pregnadien-3-ol-20-one, m.p. 178° [*oxime*, m.p. 215° (decomp.)]. J. D. R.

Autocondensation of ethyl acetoneoxalate. A. HEIKEL (Suomen Kem., 1938, 11, B, 5—7).— $\text{COMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ with warm aq. NaOAc gives a compound (I), $\text{C}_{12}\text{H}_{16}\text{O}_8$, m.p. $90\text{--}91^\circ$, converted by drying in vac. into a substance (II), $\text{C}_{12}\text{H}_{14}\text{O}_7$, m.p. 85° , which with Ba(OH)_2 yields $5:3:1\text{-OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$ (cf. Claisen, A., 1890, 364). It is suggested that (II) and (I) are *Et* 6-hydroxy-2-carboxy-4-methylbenzoylformate mono- and di-hydrate, respectively. F. R. S.

Racemisation of an optically active acid and its methyl ester. C. L. BICKEL (J. Amer. Chem. Soc., 1938, 60, 927—929).— $\gamma\text{-Keto-}\alpha\gamma\text{-diphenylpropionic acid}$ is resolved by quinine in EtOAc into the *l*- and *d*-acids, m.p. 181° , [$\alpha\text{]}_D^{25}$ 148° in MeOH, which are racemised only by hot fairly conc. alkali

or by hot conc. HBr or HI, and not by heat alone. The 1-Me ester, m.p. 52°, is racemised by very dil. alkali in H₂O or MeOH (50% in 52 hr. by 0.0002N-NaOH-MeOH at 26°; faster by more conc. NaOH) without hydrolysis; 0.38N-NaOH-MeOH also causes hydrolysis (25%).

R. S. C.

Derivatives of cyclic β -ketocarboxylic acids.—See B., 1938, 488.

Micro-organisms. LVII. Fumigatin (3-hydroxy-4-methoxy-2:5-toluquinone) and spinulosin (3:6-dihydroxy-4-methoxy-2:5-toluquinone), metabolic products respectively of *Aspergillus fumigatus*, Fresenius, and *Penicillium spinulosum*, Thom. W. K. ANSLOW and H. RAISTRICK (Biochem. J., 1938, 32, 687—696).—Fumigatin (I), m.p. 116° (acetate, m.p. 95—96°), extracted from the aerated metabolism solution with CHCl₃ after acidification (HCl), gives a purple colour with alkali, liberates I from KI, but does not react with o-C₆H₄(NH₂)₂. (I) and Et₂O-CH₂N₂ yield a compound, C₁₀H₁₂O₄N₂, m.p. 93° (probably a pyrazole); Me₂SO₄-K₂CO₃-COMe₂ afford the Me₂ ether, m.p. 59°, whilst reduction (Na₂S₂O₄) gives 3-hydroxy-4-methoxy-2:5-toluquinol, m.p. 100—101°, also present in the metabolism solution. The Ag salt of (I) with EtI yields 4-methoxy-3-ethoxy-2:5-toluquinone, reduced to the quinol, m.p. 55—56°. 5-Nitro-3-methoxy-4-ethoxytoluene, m.p. 59° (from 5-nitrocreosol, Et₂SO₄, and K₂CO₃ in PhMe), when reduced (Sn + HCl) yields the NH₂-compound, oxidised (Na₂Cr₂O₇, dil. H₂SO₄) to 3-methoxy-4-ethoxy-2:5-toluquinone, m.p. 50°, reduced to the quinol, m.p. 64° (different from the above quinol). (I) with Ac₂O-conc. H₂SO₄ gives 2:3:5:6-tetra-acetoxy-4-methoxytoluene, m.p. 192—192.5°, which when hydrolysed (MeOH-H₂SO₄), and the product oxidised (air in alkaline solution), yields 3:6-dihydroxy-4-methoxy-2:5-toluquinone (spinulosin; A., 1931, 1092).

A. LI.

Isomeric dimethoxy-2:5-toluquinones and related compounds. W. K. ANSLOW, J. N. ASHLEY, and H. RAISTRICK (J.C.S., 1938, 439—442).—Methylation (Me₂SO₄-K₂CO₃-COMe₂) of 3:6-dihydroxy-2:5-toluquinone yields 3:6-dimethoxy-2:5-toluquinone, m.p. 104—105°. 6-Methoxy-2:5-toluquinone, m.p. 19—20°, with Ac₂O-H₂SO₄ yields 3:4:6-triacetoxy-2-methoxytoluene, m.p. 98—99°, hydrolysed (MeOH-H₂SO₄ in N₂) to 3:4:6-trihydroxy-2-methoxytoluene, m.p. 146—147°, which is oxidised (FeCl₃) to 4-hydroxy-6-methoxy-2:5-toluquinone, m.p. 116°, methylated to 4:6-dimethoxy-2:5-toluquinone (I), m.p. 125°. Hydrolysis of 2:3:6-triacetoxy-4-methoxytoluene with MeOH-H₂SO₄ yields 2:3:6-trihydroxy-4-methoxytoluene, m.p. 150° (decomp.), which is oxidised (FeCl₃) to 6-hydroxy-4-methoxy-2:5-toluquinone (II), m.p. 204° (lit. 186°, 183—185°), which with Me₂SO₄-K₂CO₃ yields (I). With Ac₂O-H₂SO₄, (II) does not undergo the Thiele-Winter reaction but yields 6-acetoxy-4-methoxy-2:5-toluquinone, m.p. 139°. 5-Nitrohomoveratrole when reduced (Sn-HCl-EtOH) yields 5-aminohomoveratrole, which is oxidised (Na₂Cr₂O₇-H₂SO₄) to 3:4-dimethoxy-2:5-toluquinone, m.p. 59°, identical with fumigatin Me ether prepared from fumigatin, a metabolic product

of *Aspergillus fumigatus*, Fresenius (cf. preceding abstract).

J. D. R.

Constitution of compounds formed by the oxidation of quinol in presence of ammonium sulphite or primary amines. (MLLE.) Y. GARREAU (Compt. rend., 1938, 206, 840—842).—The NH₄ salt of 2:5-diamino-*p*-benzoquinone-3:6-disulphonic acid (I) (the α -acid of A., 1936, 721) with hot H₂SO₄ (*d* 1.83) affords 2:5-diamino-*p*-benzoquinone, which indicates that the SO₃H in (I) are in *p*-positions. The β -acid (*loc. cit.*) is 2(or 5)-amino-5(or 2)-hydroxy-*p*-benzoquinone-1-imine-3:6-disulphonic acid (II). (I) with SnCl₂-HCl or Pt-H₂ affords 2:4-diaminoquinol-3:6-disulphonic acid, insol. in H₂O, whilst (II) (NH₄ salt) with Pt-H₂ gives 2:4(or 4:5)-diamino-1:5(or 1:2)-dihydroxyquinol-3:6-disulphonic acid (+H₂O), easily sol. in H₂O. The α - and β -isomerides of NH₂Bu 2:5-dibutylamino-*p*-benzoquinonemonosulphonate (cf. A., 1937, II, 338) are similarly related to one another. J. L. D.

Polymerisation of α -naphthaquinone. C. MARSCHALK (Bull. Soc. chim., 1938, [v], 5, 304—306).— α -Naphthaquinone in PhNO₂ at 50°, treated slowly with AlCl₃, gives a 65% yield of trinaphthobenzene trioxide (trisanhydrohexahydroxytrinaphthobenzene) (A., 1934, 185).

E. W. W.

New synthesis of metal salts of hydroxyanthraquinones. I. G. FLUMIANI and V. BAJTÓ (Monatsh., 1938, 71, 293—297).—1-Hydroxyanthraquinone when heated (autoclave; at the m.p.) with Cu or CuO gives its Cu salt. The reaction does not occur in absence of O₂. Zn and Cd salts are similarly prepared. Similarly 1:8-dihydroxyanthraquinone gives a Cu salt (1 Cu:2 of the anthraquinone), identical with that prepared with Cu(OAc)₂-EtOH (Mangini, A., 1932, 164), and Cu salts of the following have been prepared: 1:2- and 1:5-di-, 1:2:3-, 1:2:6-, and 1:2:7-tri-, 1:2:5:8-tetra-, and 1:2:3:5:6:7-hexahydroxyanthraquinone. No salts (Cu, Zn, or Cd) could be obtained from 2-mono-, 1:4-, 2:6-, and 2:7-di-, or 1:2:4-tri-hydroxyanthraquinone.

H. G. M.

Halogenoaminoflavanthrones and compounds of the anthraquinone series.—See B., 1938, 488.

Structure of lignin. H. HIBBERT (Canad. J. Res., 1938, 16, B, 69—71).—The theories of the structure of lignin advanced by Freudenberg and by Hilpert are considered to be insufficiently supported by experimental evidence. A scheme is advanced in which the basic lignin-building constituent is regarded as arising from the condensation of guaiacol (I) with fructose or one of its derivatives. Lignin is thus a condensation product of (I) with a γ -keto-hydroxypentanol.

H. W.

Lignin and related substances. XXX. Formation of formaldehyde from lignin induced by acids. M. J. HUNTER, G. F. WRIGHT, and H. HIBBERT. XXXI. Aromatic and non-aromatic portions of lignin. A. BELL, A. B. CRAMER, G. F. WRIGHT, and H. HIBBERT (Ber., 1938, 71, [B], 734—745, 746—755).—XXX. Hexoses which contain the groups OH·C(CH₂·OH)·O·, CH(CH₂·OH)·O·, or OH·CH·CH(OH)·O give small amounts of CH₂O and

furfuraldehyde (I) when boiled with dil. acids (HCl; 28% H_2SO_4). The yields depend on the experimental conditions. Under the same conditions, quant. or very good yields of CH_2O are obtained from methylenedioxy-compounds such as piperonal, safrole, or piperonylic acid. Lignin (II) preps. obtained by various known processes of extraction give varying amounts of CH_2O and (I) when boiled with the same acids under the same conditions. A substance containing the CH_2O_2 -ring yields little or no CH_2O under the conditions customary for the isolation of lignin. The presence of the CH_2O_2 group in (II) is not therefore confirmed and the results point to the presence of a carbohydrate or its decomp. product chemically united to (II). The yield of CH_2O diminishes as this is more completely removed, e.g., by use of HCO_2H as extracting agent, by methylation, etc.

XXXI. Anhyd. HCO_2H is unsuitable for the extraction of wood since it causes deep-seated changes in addition to formylation. The differences between (II) obtained with 100% and 93% HCO_2H are possibly caused by combined carbohydrate. Treatment of glucose, fructose, sucrose, etc. with HCO_2H or AcOH gives (II)-like products in 1–35% yield. They are insol. in H_2O , sol. in dil. alkali. The solubility in org. media is similar to that of the less freely sol. (II). A further analogy exists between "fructose humic acids" (III) and similarly prepared (II) since in each case all the OH groups which can be methylated are acidic in character. The CO content of (III) is considerably > that of (II) with similar Ac or CHO content. More distinct differences are observed in the solubilities of the methylated products. Some of the most highly methylated products of (II) are sol. in light petroleum whereas (III) is transformed by CH_3N_2 into products insol. in all media. Oxidation of (I) does not give veratric acid. Further evidence of the presence of aromatic groups in (II) is found in the formation of EtI in addition to MeI when birch-(I) (obtained by HCO_2H or AcOH) is treated with HI. This does not indicate the presence of OEt but probably arises from a reductive decomp. of (II). It is concluded that (I) is neither exclusively aromatic nor exclusively non-aromatic but belongs to both types and consists of an aromatic and a carbohydrate component.

H. W.

Lignin and related compounds. XXXIII. Isolation of acetovanillone from waste sulphite pulp liquor. I. K. BUCKLAND, G. H. TOMLINSON, and H. HIBBERT (Canad. J. Res., 1938, 16, B, 54–56).—Waste sulphite pulp liquor when treated with aq. alkali gave vanillin (I), acetovanillone (II), phenolic substances, and a tarry, resinous product. The yield of (II) is about 5.5% of that of the (I) formed or about 0.3% calc. on the basis of the lignin present.

H. W.

Lignin and related compounds. XXXIV. Acetovanillone and acetosyringone as degradation products of ligninsulphonic acids. F. LEGER and H. HIBBERT (J. Amer. Chem. Soc., 1938, 60, 565–567).—Purified spruce ligninsulphonic acid and hot aq. alkali give 6.4% of vanillin and 0.27% of acetovanillone. Birch ligninsulphonic acid gives

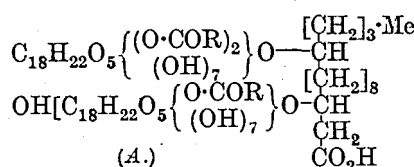
5.8% of vanillin and syringaldehyde and 0.84% of acetosyringone (I) (all yields are calc. on the wt. of lignin used). It is suggested that these products arise by the reactions $\cdot\text{CAr}(\text{OH})\cdot\text{CH}_2\cdot\text{CHAR}\cdot$ (A) \rightarrow $\text{COAr}\cdot\text{CH}_2\cdot\text{CHAR}\cdot \rightarrow \text{COAr}\cdot\text{CH}_2\cdot\text{CHAR}\cdot\text{OH} \rightarrow \text{COArMe} + \text{ArCHO}$; they are incompatible with Freudenberg's formulæ. The fragment (A) is considered to be a degradation product of lignin, which is itself formed from fructose and guaiacol. (I) (*p*-nitrophenylhydrazone, new m.p. 194.5–195.5°) is prepared by rearrangement of 1:3:4- $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{OAc}$ by AlCl_3 in PhNO_2 .

R. S. C.

Isolation of guaiacol from waste sulphite liquor. F. LEGER and H. HIBBERT (Canad. J. Res., 1938, 16, B, 68).—The acetylvanillone (I) from waste sulphite liquor from soft woods is a degradation product of pure ligninsulphonic acid. The volatile phenolic oil has been identified as guaiacol (II) by its b.p., its *p*-nitrobenzoate and *p*-toluenesulphonate. The ratio of (I):(II) is approx. 4:1.

H. W.

Jalap resin and its main constituent, convolvulin. C. MANNICH and P. SCHUMANN (Arch. Pharm., 1938, 276, 211–226).—Convolvulin (I) is a substance of high mol. wt. and colloidal character, insol. in H_2O but freely sol. in H_2O containing less NaOH than corresponds with its small acid val. The nearly neutral solution has a foul taste and strongly attacks the mucous membrane of the throat. It does not diffuse through parchment or Cellophane, is pptd. by salt solutions, and becomes cloudy when warmed. The neutral solution has full purgative action. Excess of NaOH hydrolyses (I) rapidly whereby the solution loses its colloidal character, unpleasant taste, and physiological activity. Alkaline hydrolysis of (I) affords rhamnoconvolvulic acid (II) (74%), tiglic acid (9%), *exogonic acid*, $\text{C}_{10}\text{H}_{16}\text{O}_4$ (III), b.p. 175°/10 mm., $[\alpha] \pm 0^\circ$ (7%), $\text{Bu}^n\text{CO}_2\text{H}$ (7.6%), and $\text{CHMeEt}\cdot\text{CO}_2\text{H}$ (1.4%). Votocek's observation that (II) is $\beta\alpha$ -dihydroxypalmitic acid linked with two trisaccharide residues each of which can be hydrolysed to 2 mols. of glucose and 1 mol. of rhamnose is confirmed (A., 1929, 541, 543) and the structural unit (A) of (I) is formed from it by esterification of three (or four) OH of the sugar residues by the volatile acids



and ester-like joining of these larger mols. by a OH of one with a CO_2H of another mol. (III) is monobasic, and contains 1 active H (Zerevitinov) but no OMe. It is not hydrogenated (PtO_2 or Pd-C) at room temp. and pressure. Br in HCl_3 is decolorised with evolution of much HBr . Reduction with Na and EtOH gives highly fluorescent, dark, non-volatile products. Ac_2O and NaOAc give a viscous resin. Reaction does not occur with carbonyl reagents. Oxidation with KMnO_4 in alkaline solution yields (?) EtCO_2H and a liquid acid, b.p. 170–190°/15 mm. (partial decomp.). The Ag salt and Me ester, b.p. 128–130°/14 mm., of (III) are described. Conc. HI and red P transform (III) into an acid, $\text{C}_{10}\text{H}_{16}\text{O}_3\text{I}_2$, m.p. 80–81°.

H. W.

Soya-bean saponins. III. K. TSUDA and S. KITAGAWA (Ber., 1938, 71, [B], 790—797; cf. A., 1938, II, 24).—Soya-sapogenol *D* gives a *diformate*, m.p. 231°, *diacetate*, m.p. 192°, and *dibenzoate*, m.p. 240°. It is indifferent towards ketonic reagents and cannot be catalytically hydrogenated. It contains therefore only 2 OH, the remaining O being probably in etheral union. Soya-sapogenol *B* (I) yields a *triformate*, m.p. 218°, and soya-sapogenol *C* a *diformate*, m.p. 263°, confirming thus the presence of 3 OH and 2 OH, respectively. When titrated with $\text{Pb}(\text{OAc})_4$ (1) slowly absorbs 1 O; ketone or aldehyde could not be obtained and half the original substance is isolated from the product. The presence of an α -glycol is therefore unlikely. Oxidation of (I) with CrO_3 in AcOH gives a neutral substance, $\text{C}_{29}\text{H}_{44}\text{O}_2$, m.p. 254—256° (*dioxime*, decomp. 266°; *dihydrazone*, decomp. 205°), indicating the presence of a primary OH (oxidised to CO_2H and lost as CO_2) and 2 sec. OH. Similar observations have been made with hederagenin

Me ester and bromohederagenolactone; the ring A characteristic of hederagenin appears also present in (I). Further confirmation of the presence of an inactive, non-hydrogenatable double linking in (I) is found in the conversion of its triacetate (II) by BzO_2H into an *oxide*, $\text{C}_{30}\text{H}_{47}\text{O}(\text{OAc})_3$, decomp. 213°. Oxidation of (II) by CrO_3 -AcOH or by H_2O_2 gives an isomeric *oxide*, $\text{C}_{30}\text{H}_{47}\text{O}(\text{OAc})_3$ (III), m.p. 258°, which does not give a coloration with $\text{C}(\text{NO}_2)_4$ and could not be acetylated or oximated. When hydrolysed with 0.1N-KOH it gives 3 AcOH and a neutral *deacetyl* derivative, m.p. 254°, which, like (II), is very resistant towards catalytic hydrogenation. It appears probable that (III) is a ketone related to (II) in the same manner as Me ketoacetyldihydro-oleanolate is to Me acetyloleanolate. In confirmation, oxidation of (II) with HNO_3 yields a *triacytyldicarboxylic acid*, $\text{C}_{36}\text{H}_{56}\text{O}_{10}$, decomp. 293° (corresponding *anhydride*, m.p. 283°). H. W.

Constitution of resin phenols and their biogenetic significance. VI. Degradation of pinoresinol dimethyl ether or eudesmin with permanganate and with nitric acid. H. ERDTMAN (Svensk Kem. Tidskr., 1938, 50, 68—72; cf. A., 1937, II, 28, 69).—Dibromopinoresinol Me₂ ether with HNO_3 in AcOH at 10° yields 4-bromo-5-nitroveratrole (80% yield). KMnO_4 in COMe_2 oxidises pinoresinol Me₂ ether or eudesmin to 1:2:4- $\text{C}_6\text{H}_3(\text{OMe})_2\text{CO}_2\text{H}$ (60%). HNO_3 in AcOH oxidises $\text{CHPh}[\text{C}_6\text{H}_2(\text{OMe})_3]_2$ to PhCHO (75%) and 1:2:4:5- $\text{NO}_2\text{C}_6\text{H}_2(\text{OMe})_3$ (80%). A. LI.

Yellow pigment from the osage orange (*Mac-lura pomifera*, Raf.). E. D. WALTER, M. L. WOLFROM, and W. W. HESS (J. Amer. Chem. Soc., 1938, 60, 574—577).—The fruit, previously extracted with light petroleum, yields to Et_2O 5.8% of *osajin*, $\text{C}_{24}\text{H}_{22}\text{O}(\text{CO}_2)(\text{OH})_2$, m.p. 189°, 193° (corr.), α 0°, which is an *o*-dihydric phenol, since it reduces Fehling's solution, gives a Ag mirror with hot Tollens' reagent in $\text{C}_5\text{H}_5\text{N}$, gives a green FeCl_3 colour, is sol. in NaOH, and gives a *mono*-, m.p. 159° (green FeCl_3 colour), and *di-acetate*, m.p. 152° (no FeCl_3 colour).

With a little H_2SO_4 or HCl in AcOH it gives a deep orange colour. It gives no CO derivative and with HNO_3 affords only $\text{H}_2\text{C}_2\text{O}_4$. Its absorption spectrum has a single max. at 2750 Å. Its behaviour with alkali indicates lactonic structure. It gives a non-reducing *di-p-toluenesulphonate*, m.p. 148°, which, since it gives a green FeCl_3 colour, probably contains a different lactone structure. R. S. C.

Constituents of pyrethrum flowers. XI.
Chrysanthin. W. G. ROSE and H. L. HALLER (J. Org. Chem., 1938, 2, 484—488; cf. A., 1938, II, 151).—Light petroleum extracts of pyrethrum flowers often deposit <0.1% of *chrysanthin*, $\text{C}_{17}\text{H}_{22}\text{O}_5$, m.p. 177—178°, $[\alpha]_D^{20}$ -30.5° in CHCl_3 , which with P_2O_5 in EtOH gives *dihydrochrysanthin*, m.p. 205—208°, is oxidised by CrO_3 -AcOH to *dehydrochrysanthin*, $\text{C}_{17}\text{H}_{20}\text{O}_5$, m.p. 175—177°, gives a small yield of a phenol on KOH-fusion, and with warm 5% NaOH yields AcOH and an acid, $\text{C}_{15}\text{H}_{25}\text{O}_6\cdot\text{OH}$, m.p. 190—192°. This acid is acetylated by $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$, but no acetate was isolated; at 112°/vac. it gives H_2O and an acid, $\text{C}_{15}\text{H}_{24}\text{O}_6$, m.p. 210—211°. R. S. C.

Pyroabietic acid. E. E. FLECK and S. PALKIN (J. Amer. Chem. Soc., 1938, 60, 921—925).—Pyroabietic acid, prepared from *l*-abietic acid by Pd-C, is a product of disproportionation (cf. Fieser *et al.*, A., 1938, II, 108); prepared at 225° it contains dehydro- (I), dihydro-, m.p. 129—130°, $[\alpha]_D^{20}$ -3° in abs. EtOH (Me ester, an oil), and *tetrahydroabietic acid*, m.p. 183—184°, $[\alpha]_D^{20}$ +6° in abs. EtOH (Me ester, m.p. 44—45°), saturated to $\text{C}(\text{NO}_2)_4$; when prepared at 275° it gives mainly (I), much gas being liberated. R. S. C.

Eschscholtzcanthin from petals of the Californian poppy.—See A., 1938, III, 544.

Preparation and properties of derivatives of 2-aminofuran. H. M. SINGLETON and W. R. EDWARDS, jun. (J. Amer. Chem. Soc., 1938, 60, 540—544).—2-Furoyl chloride and NaN_3 in Et_2O at 0° give 91.6% of the azide, which, when cautiously heated in Ph_2O under N_2 or CO_2 , gives 73.4% of 2-furylcarbimide (I), b.p. 111—112°/760 mm., 54°/40 mm. This is foul-smelling, lachrymatory, and toxic. Reactions with it are conducted under N_2 . The azide and C_6H_6 or distilled (I) and MgPhBr give 2-benzamidofuran, m.p. 89—92°, hydrolysed to BzOH, NH_3 , and tars; crude (I) yields also a little 2-furoanilide, inseparable from the main product. With MgEtBr (I) gives 2-propionamidofuran, m.p. 80.5—81°, b.p. 134°/14 mm., hydrolysed to EtCO_2H and NH_3 . 2-Aminofuran could not be isolated. 35% KOH at 50° converts (I) into *K* 2-furylcarbamate (81.8% yield), cryst.; $\text{Ba}(\text{OH})_2$ gives a worse yield of the *Ba* salt; the *K* salt with Me_2SO_4 -NaOH gives the Me ester, b.p. 115—120°/18 mm. With H_2O at 5° (I) gives (?) furylcarbamic acid, which decomposes spontaneously into *s-di-2-furylcarbamide*, m.p. 190° (decomp.). R. S. C.

Conversion of furfuryl alcohol into lævulic acid. F. LEGER and H. HIBBERT (Canad. J. Res., 1938, 16, B, 68—69).—The following scheme is proposed in explanation of the conversion of furfuryl alcohol into

Melævulate by HCl-MeOH: $\begin{array}{c} \text{CH}\cdot\text{CH} \\ \text{CH}-\text{O} \end{array} \rightarrow \text{C}\cdot\text{CH}_2\cdot\text{OH} \rightarrow$
 $\begin{array}{c} \text{CH}\cdot\text{CH} \\ \text{OH}\cdot\text{CH}-\text{O} \end{array} \rightarrow \text{CH}\cdot\text{CH}_2\cdot\text{OH} \rightarrow \begin{array}{c} \text{CH}\cdot\text{CH} \\ \text{OH}\cdot\text{CH}-\text{O} \end{array} \rightarrow \text{C}\cdot\text{CH}_2$
 $\rightarrow \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{CO}-\text{O} \end{array} \rightarrow \text{C}\cdot\text{CH}_2 \text{ or } \begin{array}{c} \text{CH}_2\cdot\text{CH} \\ \text{CO}-\text{O} \end{array} \rightarrow \text{CMe} \rightarrow$
 $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ or $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{CO}-\text{O} \end{array} \rightarrow \text{CMe}\cdot\text{OH}$. The same mechanism explains the production of lævulic acid from hydroxymethylfurfuraldehyde and of γ -ketopimelic acid from furoylacrylic acid. H. W.

Furan derivatives. V. I. J. RINKES (Rec. trav. chim., 1938, 57, 390—394; cf. A., 1932, 519).—3-Nitro-2-carboxylic acid, m.p. 125°, prepared by oxidising the 2-Mc derivative with $\text{K}_3\text{Fe}(\text{CN})_6\text{-KOAc}$, is decarboxylated with Cu chromite- $\text{C}_6\text{H}_7\text{N}$ at 150° into 3-nitro-2-styrylfuran-5-carboxylic acid, m.p. 237°, similarly yields 3-nitro-2-styrylfuran, m.p. 135°. 5-Nitro-2-carboxylic acid is isolated from the products of ozonisation of Et 5-nitro-2-furfurylacrylate. A. T. P.

Furoylacetaryl amides.—See B., 1938, 490.

Furan-substituted ethanolamines. A. LES-PAGNOL and VAN THIENEN (Bull. Sci. Pharmacol., 1938, 40, 49—59).—Furoinoxime is reduced ($\text{Zn} + \text{NaOH}$) to β -hydroxy- α -difuryl ethylamine, m.p. 104—105° (hydrochloride, m.p. 185°). Benzofuroinoxime is reduced ($\text{Zn} + \text{HCl}$) to β -hydroxy- β -phenyl- α -furyl ethylamine, m.p. 106—107°. PhCHO and glycine in EtOH-NaOH when treated with furfuraldehyde yield the furfurylidene derivative, m.p. 119°, of β -hydroxy- β -furyl- α -phenylethylamine, m.p. 123°. A. LI.

2:5-Dimesityl- and 2:5-di(bromomesityl)-furan. R. E. LUTZ, (MISS) E. C. JOHNSON, and J. L. WOOD (J. Amer. Chem. Soc., 1938, 60, 716—718).— $(\text{C}_6\text{H}_3\text{Me}_3\cdot\text{CO}\cdot\text{CH})_2$ (I) is rapidly reduced by Sn-HCl-AcOH to $(\text{C}_6\text{H}_3\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2)_2$ (II), also obtained by $\text{H}_2\text{-Pd-CaCO}_3$. (II) resists further reduction, is unaffected by conc. aq. HCl, gives tars with AcCl , and is converted by $\text{Ac}_2\text{O-H}_2\text{SO}_4$ into a SO_3H -derivative, m.p. about 230° (decomp.). Long treatment of (I) with Sn-HCl-AcOH affords some 2:5-dimesitylfuran, m.p. 82—83° (corr.) [NO_2 -derivative, m.p. 107.5—108° (corr.)], which is obtained from (II) by $\text{HCl-Et}_2\text{O}$, 85% H_3PO_4 , or, best, HI (d 1.7), is stable to Na-EtOH , with 4 Br in CCl_4 gives the 3:4- Br_2 -derivative, m.p. 146.5—147°, and with Br-FeBr_3 in CS_2 gives a Br_5 -derivative. α -Diketo- α -di-3-bromomesityl- Δ^8 -butene, m.p. 228—230°, obtained in 50% yield from fumaryl chloride, $\text{C}_6\text{H}_3\text{Me}_3\text{Br}$, and AlCl_3 in CS_2 , is reduced by Zn-AcOH to α -diketo- α -di-3-bromomesitylbutane, m.p. 183—184°, which with HI (d 1.7) at 182—185°, but not with $\text{Ac}_2\text{O-H}_2\text{SO}_4$ or HI-AcOH , gives 2:5-di-3'-bromomesitylfuran, m.p. 92—94°. R. S. C.

Hydrogenation of pyrones. R. MOZINGO and H. ADKINS (J. Amer. Chem. Soc., 1938, 60, 669—675).—Hydrogenations give least amounts of by-products when reaction is rapid, but the temp. should be as low as possible. Over $\text{Cu-Cr}_2\text{O}_3$ at 120—125°/100—200 atm. γ -pyrone gives 50% of tetrahydropyran-4-ol, b.p. 119—120°/23 mm. (3:5-dinitrobenzoate, m.p.

98—99°), and 23% of tetrahydro- γ -pyrone (better obtained with Raney Ni at a lower temp.). 2-Ethylchromone [prep. from $o\text{-OH-C}_6\text{H}_4\cdot\text{COMe}$ (modified prep.), EtCO_2Et , and Na in xylene], m.p. 20—20.5°, b.p. 124—126°/2 mm. (2:4-dinitrophenylhydrazone, m.p. 249—250°), with $\text{H}_2\text{-Cu-Cr}_2\text{O}_3$ gives 2-ethylchromanone (I), b.p. 115—116°/2 mm. (2:4-dinitrophenylhydrazone, m.p. 221—222°), 2-ethylchroman-4-ol (II), b.p. 137—139°/3 mm., m.p. 78—79° (3:5-dinitrobenzoate, m.p. 141—142°), 2-ethylchromen-4-ol (not obtained pure; gives 2-ethylbenzopyrylium platinichloride, m.p. 165—166°), 2-ethylchroman (III), b.p. 130—131°/26 mm., and $o\text{-C}_5\text{H}_{11}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, the relative yields depending greatly on the conditions. By using Raney Ni 30% of (I) or 77% of (II) may be obtained. Nitrogenation of (III) gives 90% of 2-ethylhexahydrochroman, b.p. 96—97°/18 mm. Hydrogenation of flavone [modified prep. in about 60% yield from EtOBz and $o\text{-OH-C}_6\text{H}_4\cdot\text{COMe}$ by way of $o\text{-OH-C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COPh}$, m.p. 119—120° (2:4-dinitrophenylhydrazone, m.p. 119—120°; acetate, m.p. 118—118.5°)] (2:4-dinitrophenylhydrazone, m.p. 282—283°) is less easy; with Ni at 85° it gives 20% of β -flavan-4-ol (IV), and with $\text{Cu-Cr}_2\text{O}_3$ also some flavanone (2:4-dinitrophenylhydrazone, m.p. 254—255°) and flavan-4-ol (identified by conversion into flavylium platinichloride, m.p. 199—200°). Flavanone is smoothly hydrogenated in presence of $\text{Cu-Cr}_2\text{O}_3$ to (IV), flavan, and o - γ -phenylpropylphenol (3:5-dinitrobenzoate, m.p. 143—143.5°), yields depending greatly on the conditions. Further hydrogenation of (IV) is smoothly effected with $\text{Cu-Cr}_2\text{O}_3$ at 160—170°. 7-Hydroxy-3-phenyl-2-methylchromone, m.p. 242—243°, with $\text{H}_2\text{-Cu-Cr}_2\text{O}_3$ at 120—125° gives an oily (?) mixture of alcohols, converted by hydrogenation at 131—138° into 3-phenyl-2-methylchroman-7-ol, b.p. 172—174°/0.3 mm. (3:5-dinitrobenzoate, m.p. 169—170°). Flavanol deactivates $\text{Cu-Cr}_2\text{O}_3$ and yields only 17% of 3:4-dihydroxyflavan, m.p. 123—124°, and quercetin cannot be hydrogenated with $\text{Cu-Cr}_2\text{O}_3$ or Ni, even at 200°. 2-Methylchromone with $\text{H}_2\text{-Cu-Cr}_2\text{O}_3$ at 150—155° gives 84% of 2-methylchroman-4-ol, m.p. 87—88°. R. S. C.

Derivatives of coumarin. I. 5- and 6-Methoxy-2-benzylcoumaran-3-one [4- and 5-methoxy-1-benzylbenzofuran-2-one]. R. L. SHRINER and R. E. DAMSCHRODER (J. Amer. Chem. Soc., 1938, 60, 894—896).—Hydrogenation (PtO_2 ; 2—3 atm.) of 4- and 5-methoxy-1-benzylidenbenzofuran-2-one in AcOH gives 4-, m.p. 76—77° (corr.), and 5-methoxy-1-benzylbenzofuran-2-one, m.p. 92—93° (corr.), respectively, also obtained less well by boiling with NaOAc-EtOH the condensation product from p - and m - $\text{C}_6\text{H}_4(\text{OMe})_2$, respectively, α -bromo- β -phenylpropionyl chloride (prep. from $\text{CHPhMe}\cdot\text{COCl}$ and Br at 65—70°), b.p. 113—115°/5 mm., and AlCl_3 in CS_2 . R. S. C.

Vitamin-E: structure of β -tocopherol. F. BERGEL, A. JACOB, A. R. TODD, and T. S. WORK (Nature, 1938, 141, 646; cf. A., 1938, II, 137).—5-Hydroxy-2:4:6:7-tetramethylcoumaran (I), m.p. 124—125°, has been synthesised starting from ψ -cumoquinol and allyl bromide, and 5-hydroxy-4:6:7-trimethyl-2- n -heptadecylcoumaran (II), m.p.

95—95.5°, isomeric with β -tocopherol (III), from ψ -cumoquinone and Et sodiostearoylacetate followed by partial hydrogenation of the intermediate coumarone. Both (I) and (II) are similar to (III) in absorption spectrum (data given) and reducing properties. (II) distils at 370° without charring, giving a mixture from which a trace of a quinol, m.p. 185—190° (sublimes), is obtained. These results and surface film measurements (cf. following abstract) support the view that (III) is a coumaran derivative. Side-Me determinations of (III) indicate the presence of 6 or 7 Me. The disposition of these is discussed. The structure proposed is supported by the results of oxidation; two oily fatty acids, C_{17-18} and C_{11-12} , are obtained, giving cryst. phenylphenacyl esters.

L. S. T.

Vitamin-E; structure of β -tocopherol. J. F. DANIELLI (Nature, 1938, 141, 646).— β -Tocopherol allophanate (I) and 5-hydroxy-4:6:7-trimethyl-2-*n*-heptadecylcoumarone (II) both give stable films on 0.01N-HCl; the limiting areas are 30 and 26 sq. A., respectively. Since *p*-hexadecylcyclohexanol has a limiting area of 30 sq. A., and the lactone of γ -hydroxystearic acid one of 29 sq. A., it is concluded that (I) and (II) are analogous in structure, and that in cross-section β -tocopherol cannot have a ring system > one ring in thickness measured perpendicular to the side-chain. The ring system cannot be analogous to a phenanthrene or sterol skeleton.

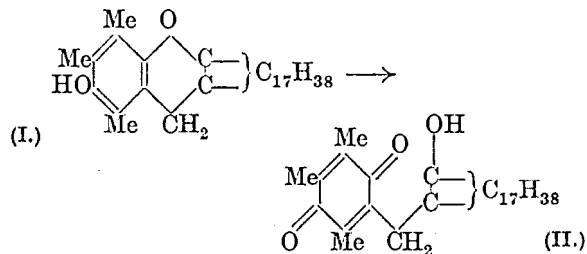
L. S. T.

Antisterility agents (vitamin-E). II. Identity of cumotocopherol and β -tocopherol. W. JOHN. **III. Fission of tocopherols with hydriodic acid.** W. JOHN, E. DIETZEL, and P. GUNTHER (Z. physiol. Chem., 1938, 252, 201—207, 208—221; cf. A., 1937, III, 497).—II. The identity of cumotocopherol and β -tocopherol (I) is established by their equal physiological activity, by the m.p. and mixed m.p. of the allophanates (sintering 144°, m.p. 145—145.5°, and clear at 145.5—146.5°), by $[\alpha]_D$ (+5.7° to +6.7° in $CHCl_3$), and by the ultra-violet absorption spectra of the allophanates. Analysis of the allophanate and the *p*-nitrobenzoate, m.p. 38—40°, shows (I) to be $C_{28}H_{48}O_3$.

III. Duroquinol, $C_{16}H_{33}Br$, and NaOH in EtOH and N_2 yield the mono- (II), m.p. 99.5° (allophanate, m.p. 208°), and di-cetyl ether, m.p. 90.5°. Similarly are prepared the mono-, m.p. 133°, and di-benzyl, m.p. 143°, mono- (III), m.p. 98°, and di-dodecyl, m.p. 83°, and *Pr*², ether, m.p. 90—91°. From ψ -cumoquinol are prepared the mono- (IV), m.p. 89° (allophanate, m.p. 180°), and di-cetyl ether, m.p. 60.5°. Fission of (II) with AcOH-HBr yields duroquinone (V) and $C_{12}H_{25}OH$, whilst α -tocopherol (VI) and cumotocopherol [= (I)] are only slightly attacked. With HI (d 2.0) in Ac_2O -AcOH, (VI) yields 2:3:5:1- $C_6H_3Me_3OH$ (VII), whilst (I) gives *p*-xylenol and a substance [dinitrobenzoate (probably $C_{16}H_{14}O_6N_2$), m.p. 142°]. Similarly, with HI- Ac_2O -AcOH, (II) or duroquinol yields durenol, whilst (IV) yields (VII). When heated at 350° in N_2 , (II) gives duroquinol, and (IV) yields ψ -cumoquinol. Oxidation ($AcOH-H_2CrO_4$) of (II) yields (V) and palmitic acid. Ultra-violet absorption spectra for most of the above compounds are given.

J. D. R.

Constitution of α -tocopherol. W. JOHN (Z. physiol. Chem., 1938, 252, 222—224).—Oxidation of α -tocopherol (I) with $AgNO_3$ or $FeCl_3$, followed by chromatographic adsorption, yields α -tocopherylquinone (II), $C_{29}H_{50}O_3$ (which shows a similar absorption spectrum to duroquinone), reduced to α -tocopherylquinol (triacetate, m.p. 75°). The oxidation is formulated:



J. D. R.

Coumarins.—See B., 1938, 488.

Anthocyanin pigment in the rind of sugar-cane (Purple mauritius). C. J. D. RAO, D. G. WALAWALKAR, and B. S. SRIKANTAN (J. Indian Chem. Soc., 1938, 15, 27—30).—From the aq. extract of this rind is obtained brownish-red *mauritinin chloride*, $+4H_2O$ (violet in Na_2CO_3 or $FeCl_3$ -EtOH), hydrolysed to 2 mols. of glucose and *mauritidin sulphate*, $+H_2O$, m.p. >300°, which is converted by HI into a substance believed from colour reactions to be delphinidin. *Mauritidin* contains 1 OMe and may be amplexosidin; *mauritinin* is its diglucoside.

R. S. C.

Condensation and polymerisation of $\alpha\beta$ -unsaturated aldehydes and acids. I. Condensation of furan with acraldehyde. S. M. SCHERLIN, A. J. BERLIN, T. A. SEREBRENNIKOVA, and F. E. RABINOVITSCH. **III. Polymerisation of acraldehyde and acrylic acid.** S. M. SCHERLIN, A. J. BERLIN, T. A. SEREBRENNIKOVA, and F. E. RABINOVITSCH (J. Gen. Chem. Russ., 1938, 8, 7—15, 22—34; cf. A., 1938, II, 234).—I. $CH_2=CH\cdot CHO$ (I) and furan with quinol (1 hr. at 100° in an autoclave) yield 2:5-di-(β -formylethyl)furan, m.p. 41—42° (dioxime, m.p. 132—133°), and β -2-furylpropaldehyde, oxidised by $AgNO_3$ in aq. NaOH to β -2-furylpropionic acid (*Me* ester, b.p. 89°/15 mm.). The reaction is catalysed by SO_2 , but not by HCO_2H , AcOH, pyromucic acid, H_2S , or H_2SO_4 .

III. (I) in C_6H_6 with quinol, heated at 170° for 5 hr., yields a dimeride, shown to be 3-formyl-2:3-dihydro-1:4-pyran (II), b.p. 40—40.5°/10 mm., 146°/760 mm., the semicarbazone, m.p. 123°, of which is hydrogenated (Pd catalyst) to the semicarbazone, m.p. 154°, of 3-formyltetrahydropyran (III). The oxime, b.p. 101—102°/10 mm., of (II) similarly yields the oxime, b.p. 102—104°/8—9 mm., of (III), from which the corresponding nitrile, b.p. 77°/15 mm., is obtained by heating with Ac_2O ; this is hydrolysed by HCl in EtOH at 0° to the *Et* ester, b.p. 101—103°/19—20 mm., of tetrahydropyran-3-carboxylic acid. (II) in Et₂O and MgPhBr yield 3-(2:3-dihydro-1:4-pyranyl)phenylcarbinol, b.p. 166°/20 mm. (II) is oxidised ($AgNO_3$ in aq. NaOH) to 2:3-dihydro-1:4-pyran-3-carboxylic acid (*Na* salt, $+H_2O$). Acrylic acid, heated in furan or C_6H_6 solution at 160° for 5

The method of separating the precursor of (II) from *Derris* extract and its subsequent purification, with crystallographic data, are described. The substance is 1- α -toxicarol (V), m.p. 101–102°, $[\alpha]_D^{25} -53^\circ$ in C_6H_6 + 69°, in $COMe_2$ (monoacetate, m.p. 158°) (cf. Tattersfield, B., 1937, 728). Monoacetylsumatrol has m.p. 217°. The rotation of (V) in $MeOH-KOH$ rises to +350° and falls to 0° [conversion into (II)]. Reduction (PtO_2-H_2) of (V) gives 1-dihydro- α -toxicarol, m.p. 178–180°, $[\alpha]_D^{25} -57^\circ$ in C_6H_6 (*Ac* derivative, m.p. 184–186°, $[\alpha]_D^{25} +64.5^\circ$ in $COMe_2$). (V) and (II) yield the same apotoxicarol. The change of sign of rotation is discussed with reference to the active centres of (V).

Changes in rotation and absorption spectra in the presence of alkali indicate that enolisation is easier in the toxicarol than in the rotenone series. In all cases one form of ring-junction is greatly favoured. A system of nomenclature of the stereoisomerides of (I) is formulated.

F. R. S.

Coumarino-2'-pyrones. E. SPÄTH and P. H. LÖWY (Monatsh., 1938, 71, 365–372).—Umbelliferone is converted by malic acid and conc. H_2SO_4 at 100° into a mixture of coumarino-7 : 6-2'-pyrone (*lin.-dicoumarin*) (I), m.p. 342° (vac.; corr.), and coumarino-7 : 8-2'-pyrone (*ang.-dicoumarin*) (II), m.p. 270° (vac.). 2 : 4-(OH) $_2C_6H_3 \cdot CHO$ is transformed by $CHCl_3$ and $NaOH$ into resorcinol-2 : 4-dialdehyde, m.p. 127°, converted by anhyd. $NaOAc$ and boiling Ac_2O into (II), which is also obtained from 7-hydroxycoumarin-8-aldehyde, $NaOAc$, and Ac_2O (cf. Rangaswami *et al.*, A., 1938, II, 27). Successive treatments of (I) with $NaOH-Me_2SO_4$, $KOH-KMnO_4$, and CH_2N_2 afford Me_2 4 : 6-dimethoxyisophthalate. Similar treatment of (II) gives 2 : 4-dimethoxyisophthalic acid, identified as the dianilide, m.p. 208–209°. Phloroglucinol, malic acid, and conc. H_2SO_4 give coumarino-5 : 6-7 : 8-di-2'-pyrone (III), m.p. 369° (vac.; corr.; decomp.).

H. W.

Dyes derived from acenaphthenequinone. VI. 2-(4-Methylthionaphthen)acenaphthylene-indigos [3-keto-4-methyl-2-7'-ketodihydroacenaphthylidenedihydrothionaphthens]. S. K. GUHA (J. Indian Chem. Soc., 1938, 15, 20–26; cf. A., 1936, 861).—2 : 1 : 3-CN $\cdot C_6H_3Me \cdot N_2Cl$, when treated with K xanthate and K_2CO_3 and then with $CH_2Cl \cdot CO_2Na$, gives 2 : 1 : 3-CN $\cdot C_6H_3Me \cdot CH(SH) \cdot CO_2H$ (Na salt), which, when distilled in steam from acid solution, gives 3-hydroxy-4-methylthionaphthen, m.p. 75–76°. With acenaphthenequinone or its derivatives and $HCl-AcOH$ this gives 3-keto-4-methyl-2-7'-keto-, m.p. 263°, -2-3'-chloro-7'-keto-, m.p. 270–271° after sintering, -2-3'-bromo-7'-keto-, m.p. 260°, and -2-7'-keto-1'-methoxy-dihydroacenaphthylidenedihydrothionaphthen, m.p. >305°. The colours, absorption spectra, and dyeing properties of these dyes show that the effect of 4-Me is intermediate between those of 5- and 6-Me in this series.

R. S. C.

Thioaldehydes and thioketones. II. S. K. MITRA (J. Indian Chem. Soc., 1938, 15, 59–64).—Passage of H_2S through a solution of Bz_2 in $HCl-EtOH$ at 14° or in $AcOH-aq. HCl$ gives tetraphenyl-

2 : 5-endosulphidothiophen (I), $\begin{array}{c} CPh-CPh \\ || \quad S < \quad \\ CPh-CPh \end{array} S$, m.p.

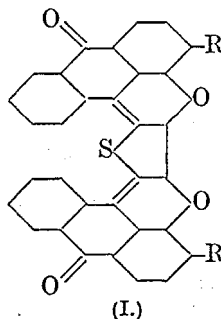
195°, which gives the thiophen reaction with isatin- H_2SO_4 , is unaffected by $Zn-HCl$, and slowly attacked by $KMnO_4$, and gives a $SS'-Br_4$ -derivative, m.p. 139°, which regenerates (I) in boiling $EtOH$ or $AcOH$. With HI (I) gives tetraphenylthiophen. In $EtOH-HCl$ at 0° Bz_2 and H_2S give dithiobenzil (II), m.p. 97° (formed by way of $SH \cdot CHPh \cdot CPh$), and 3-ethoxy-tetraphenyl-3 : 4-dihydro-2 : 5-endosulphidothiophen (III), m.p. 126°. Hot $HCl-EtOH$ converts (III) into (II). With Br (II) gives HBr and 4-bromo-3-ethoxy-tetraphenyl-3 : 4-dihydro-2 : 5-endosulphidothiophen, m.p. 178°. $OEt \cdot CHPh \cdot CPh$ and H_2S in $HCl-EtOH$ or $-MeOH$ give (I), (II), and (III); $OMe \cdot CHPh \cdot CPh$ gives similarly in $MeOH$ (I) and 3-methoxytetraphenyl-3 : 4-dihydro-2 : 5-endosulphidothiophen. In $MeOH-HCl$ at 15° Bz_2 and H_2S give (I) and 3-hydroxytetraphenyl-3 : 4-dihydro-2 : 5-endo-oxidothiophen, $\begin{array}{c} CPh-CPh \\ || \quad O < \quad \\ CPh-CPh \end{array} S$, m.p. 165°, converted by HI at 127° into tetraphenylthiophen. $(CPhBz)_2$ and H_2S in $HCl-EtOH$ give tetraphenylfuran, m.p. 174°. $CPhBz \cdot CHBz$ and H_2S in $HCl-EtOH$ give 2 : 3 : 5-triphenyl-2 : 5-endo-oxidothiophen, m.p. 157°, and 2 : 3 : 5-triphenylthiophen, m.p. 198° (formed by way of $CSPH \cdot CHPh \cdot CH_2Bz$).

R. S. C.

Reduction products of hydroxyanthraquinones. XV. Green vat dyes from thiophen and 3-substituted 4-hydroxyanthranols. (The late) A. G. PERKIN and N. H. HADDOCK (J.C.S., 1938, 541–545).—Attempted methylation (Me_2SO_4, Na_2CO_3) of 3 : 4-dihydroxyanthranol in crude $C_6H_3Cl_3$ at 190–200° gives a green dye (I) ($R = OMe$), produced from tetrachlorothiophen in the $C_6H_3Cl_3$. 4-Hydroxy-3-methoxyanthranol and tetrachloro- or tetrabromo-thiophen in boiling $C_{10}H_8$, or 4 : 4'-dihydroxy-3 : 3'-dimethoxydianthrone with Na_2CO_3 and crude $C_6H_3Cl_3$, also yield the same dye, which is oxidised ($AcOH-H_2CrO_4$) to alizarin 2-Me ether. The *Ac* derivative, m.p. 187–189°, of 1-hydroxy-2-methylantraquinone (II) (improved prep. from 1-amino-2-methylantraquinone) is reduced ($SnCl_2-HCl-AcOH$) to 4-hydroxy-3-methylanthrone. This, with crude $C_6H_3Cl_3$ and $KOAc$, yields a green dye [(I) $R = Me$], oxidised ($AcOH-H_2CrO_4$) to (II) and a substance, $C_{24}H_{18}O_6S$, m.p. 300–303°.

J. D. R.

Preparation of pyrrolidines. G. H. COLEMAN and G. E. GOHEEN (J. Amer. Chem. Soc., 1938, 60, 730).—*N*-Chloro-amines give better yields of pyrrolidines than do *N*-bromo-amines, and dil. is better than conc. H_2SO_4 as reagent. Thus NBu_2Cl and



(I.)

n -C₅H₁₁·NMeCl give 73—75% yields of 1-butyl- and 1:2-dimethyl-pyrrolidine, respectively. R. S. C.

Catalytic transformations of heterocyclic compounds. VIII. Transformation of furanidin (tetrahydrofuran) into *N*-phenyl-, *N*-*o*-tolyl-, *N*-*p*-tolyl-, and *N*-cyclohexyl-pyrrolidine. J. K. JURIEV and G. A. MINKINA (J. Gen. Chem. Russ., 1937, 7, 2945—2949).—Tetrahydrofuran and cyclic amines, passed over Al₂O₃ at 400°, yield *N*-phenyl-, *N*-*o*-tolyl-, b.p. 103—104°/9 mm. (*picrate*, m.p. 101.5—102°), *N*-*p*-tolyl-, and *N*-cyclohexyl-pyrrolidine. R. T.

Catalytic transformations of heterocyclic compounds. IX. Synthesis of 1-phenyl-2-methylpyrrole, 1-*o*-tolyl-2-methylpyrrole, and 1-*p*-tolyl-2-methylpyrrole. J. K. JURIEV (J. Gen. Chem. Russ., 1938, 8, 116—119).—2-Methylpyrrole is passed over Al₂O₃ catalyst at 475°, in a stream of H₂, together with NH₂Ph or *o*- or *p*-C₆H₄Me·NH₂; the products are 1-phenyl-, b.p. 118—119°/14 mm., 1-*o*-tolyl-, b.p. 111.5—113°/13 mm., or 1-*p*-tolyl-2-methylpyrrole, b.p. 119—121°/10 mm. R. T.

Pyrroles derived from acetonylacetone. S. J. HAZLEWOOD, G. K. HUGHES, and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 92—102).—Acetonylacetone and aromatic amines yield the following 1-substituted derivatives of 2:5-dimethylpyrrole: (i) at room temp. in presence of a drop of HCl, followed, if necessary, by heating at 100° for 1 to 2 hr.: *Et* (no HCl), b.p. 102°/79 mm., Ph, m.p. 51—52°; CH₂Ph, m.p. 48°; *m*-C₆H₄Br, m.p. 83°; *p*-C₆H₄Br, m.p. 74—75°; *m*-CO₂H·C₆H₄, new m.p. 146°; *p*-CO₂H·C₆H₄, m.p. 196—198°; *p*-CO₂Et·C₆H₄, m.p. 87—88°; *p*-OMe·C₆H₄, m.p. 65°; *p*-OEt·C₆H₄, m.p. 63°; *p*-NH₂·CO·C₆H₄, m.p. 207°; *p*-C₆H₄Me, m.p. 46°; α -, m.p. 121°, and β -C₁₀H₇, m.p. 71°; 5-, m.p. 77°, and 8'-C₉H₆N, m.p. 143°; *o*-xenyl, m.p. 100°; 1:1'-*m*-, m.p. 106—107° and -*p*-, m.p. 253° (softens at 245°)-phenylenebis; 1:1'-(3:3'-dimethyl-4:4'-diphenylene)bis, m.p. 190°; or method (ii), in boiling EtOH-AcOH for 0.25 to 4 hr.: *o*-C₆H₄Cl, b.p. 135°/15 mm.; *m*-C₆H₄Cl, m.p. 50°; 2:5-C₆H₃Cl₂, b.p. 151—153°/16 mm.; *m*-, m.p. 84—85°, and *p*-, m.p. 145°; *NO*₂·C₆H₄; *m*-OH·C₆H₄, b.p. 178°/10 mm., m.p. 58°; *o*-CO₂H·C₆H₄, m.p. 121—122°; *m*-NH₂·CO·C₆H₄, m.p. 192°; *o*-OMe·C₆H₄, m.p. 65°; *o*-OEt·C₆H₄, b.p. 140°/10 mm.; 2:3-(OMe)₂C₆H₃, m.p. 68°; 3:4-(OMe)₂C₆H₃, m.p. 54—55°; 3:4-(OEt)₂C₆H₃, b.p. 204—205°/34 mm.; *o*-C₆H₄Me, b.p. 123—125°/22 mm.; *m*-C₆H₄Me, m.p. 55°; 2:4-C₆H₃Me₂, b.p. 136°/10 mm.; 2:5-C₆H₃Me₂, b.p. 121°/9 mm.; 5:2-NO₂·C₆H₃Me, m.p. 103—104°; α -phenylethyl, b.p. 147—149°/14 mm.; 3'-acenaphthyl, m.p. 92°; 3'-fluorenyl, m.p. 90—91°; *p*-xenyl, m.p. 65°. CO(NH₂)₂, *o*-NO₂·C₆H₄·NH₂, 2:4-C₆H₃Cl₂·NH₂, 2:4:6-C₆H₂Br₃·NH₂, *o*-NH₂·C₆H₄·CO₂Me (anthranilic acid reacts), *o*-NH₂·C₆H₄·CO·NH₂, and 6-aminoacetoveratrone do not react. A. T. P.

Exchange of hydrogen atoms between pyrrole, indole, or their methyl derivatives and water.

III. Exchange of hydrogen atoms between 1-methylpyrrole and water. M. KOIZUMI and T. TITANI (Bull. Chem. Soc. Japan, 1938, 13, 298—

304; cf. A., 1938, I, 255).—1-Methylpyrrole is unchanged in dil. D₂O-H₂O at $p_H > 3$. At lower p_H the four nuclear H are all exchanged for D slightly more readily than are those of pyrrole, in accordance with theory. R. S. C.

Exchange of hydrogen atoms between indole and water.—See A., 1938, I, 318.

Reformatsky reaction in the isatin series. F. J. MYERS and H. G. LINDWALL (J. Amer. Chem. Soc., 1938, 60, 644—645).—Isatin does not undergo the Reformatsky reaction and *O*-methylisatin gives tars and isatin. 1-Ethylisatin (I) with 1 mol. of CH₂Br·CO₂Et and 1 Zn gives 1-ethyloxindole and with 2 equivs. of each reagent gives a 76% yield of *Et* 3-hydroxy-1-ethyloxindolyl-3-acetate (II), m.p. 127—128.5°, converted by hot 50% KOH into 1-ethyl-2-quinoline-4-carboxylic acid, m.p. 205—206° (*Et* ester, m.p. 88.5—89°), also obtained from (a) (I) and CH₂(CO₂H)₂ in AcOH and (b) the amide of (I) and 50% KOH; this amide, m.p. 186.5—188.5°, is obtained from (I) by conc. aq. NH₃ at room temp. The 1-Me compounds behave similarly. *Et* hydroxy-1-methylindolylacetate, m.p. 100—101.5° (*amide*, 191.5—193.5°), is incidentally described. R. S. C.

Formation of 3-indolylacetic acid by the action of ultra-violet light on tryptophan. A. BERTHELOT and (Mlle.) G. AMOUREUX (Compt. rend., 1938, 206, 699—701; cf. A., 1937, III, 374; 1938, III, 444).—Solutions of tryptophan (0.01—0.05%) containing AcCO₂Na (0.5%) and glucose (2.5%) at p_H 6.5—6.8 in quartz vessels and in absence of air when irradiated with a Hg-vapour lamp rapidly give 3-indolylacetic acid ($\lambda > 2900$ Å. has no effect). At p_H 4.5 the reaction is retarded. In air, melanins are produced. Under aseptic conditions and without O₂, the reaction proceeds to some extent in 3 days in sunlight. J. L. D.

Synthesis of Δ^3 -tetrahydropyridine. R. R. RENSHAW and R. C. CONN (J. Amer. Chem. Soc., 1938, 60, 745—747).—4-Hydroxypiperidine (I) is obtained from 4-hydroxypyridine by Na-EtOH, but not by catalytic hydrogenation. 4-Bromopiperidine (modified prep.) and solid KOH or 4-iodopiperidine and KOH-EtOH give only (I). The Br-compound and NaOMe or NaOEt give Δ^3 -tetrahydropyridine, unstable [*hydrochloride*, m.p. 188—189° (corr.); *platini*-, m.p. 187—189° (decomp.; corr.), and *aureichloride*, m.p. 141—142° (decomp.); *dibromide hydrochloride*, m.p. 193° (decomp.; corr.), and *platini-chloride*, m.p. 216—217° (decomp.)], and 25% of 4-methoxypiperidine (only with NaOMe) [*hydrochloride*, m.p. 137.5—139.5° (corr.); *platini-chloride*, m.p. 178—178.5° (decomp.; corr.)]. The former product with MeI-Ba(OH)₂ gives 1:1-dimethyl- Δ^3 -tetrahydropyridinium iodide, m.p. 274—275° (decomp.; corr.), hydrogenated (PtO₂) to 1:1-dimethylpiperidinium iodide. R. S. C.

Preparation of γ -picoline. G. R. CLEMO and W. M. GOURLAY (J.C.S., 1938, 478—479).—2:4-Dimethylpyridine, PhCHO, and Ac₂O give a mixture of 2-styryl-4-methylpyridine (I), b.p. 160°/1 mm., m.p. 70° (*picrate*, m.p. 258°), and 2:4-distyrylpyridine, b.p. 250°/1 mm., m.p. 172—173°, separated by distillation.

Oxidation (KMnO_4) of (I) yields 4-methylpyridine-2-carboxylic acid, m.p. 136–137° (Et ester, b.p. 105°/1 mm., and its picrate, m.p. 126–127°), which when heated above its m.p. affords γ -picoline (methiodide, m.p. 149–150°). F. R. S.

Nicotinic acid derivatives. E. GRYSKIEWICZ-TROCHIMOWSKI (Arch. Chem. Farm., 1937, 3, 211–214).—The 1-methochloride, m.p. 163–165°, -methobromide, m.p. 164–166°, and -methiodide, m.p. 157–158°, of nicotindithylamide yield trigonelline when heated with Ag_2O in H_2O . Nicotinoyl chloride and $\text{NH}_4\text{Et}[\text{CH}_2]_2\text{NEt}_2$ in C_6H_6 yield the β -diethylaminoethyl-ethylamide of nicotinic acid, b.p. 193–194°/10 mm. (dimethiodide, m.p. 203–205°). Pyridine-4-carboxydiethylamide yields a 1-methiodide, m.p. 138–139°. The above new compounds are physiologically inactive. R. T.

Tautomerism of homologues of pyridine. III. Syntheses in the pyridine series. IV. Syntheses in the pyridine series. Introduction of radicals containing elements other than carbon and hydrogen. A. E. TSCHITSCHIBABIN (Bull. Soc. chim., 1938, [v], 5, 429–435, 436–442).—III. The substance previously (A., 1936, 1388) termed 2- β -phenylpropylpyridine (I) was really 2- α -phenylpropylpyridine. γ -Picoline, $\text{C}_{16}\text{H}_{33}\text{Cl}$, and NaNH_2 give 4-n-heptadecyl-, m.p. 33°, b.p. 207–210°/2.5 mm. [picrate, m.p. 115° (turbid), 185–190° (clear)], and 4- α -n-hexadecyl-n-heptadecyl-pyridine, m.p. 68°, b.p. 300–310°/2.5 mm. [picrate, m.p. 68–70° (turbid), 185–190° (clear); platinichloride], the salts of which are colloidal and hydrolyse in H_2O . α -Picoline gives only 2-n-heptadecylpyridine, m.p. 23.5°, b.p. 206°/2.5 mm. (picrate, m.p. 87°); it does not react with cyclopentyl chloride at room temp., and with cyclohexyl chloride gives much cyclohexene and a little 2-hexahydrobenzylpyridine, b.p. 135°/22 mm. (platinichloride, decomp. 183–185°). 4-Hexahydrobenzyl-, b.p. 266° [picrate, m.p. 172°; platinichloride, m.p. 243° (decomp.)], and 2- γ -phenyl- α - β' -phenylethylpropylpyridine, b.p. 212°/2.5 mm. (picrate, m.p. 102°), and (I), b.p. 140°/0.1 mm. (picrate, m.p. 108.5°), are prepared. At high temp. 2-cyclopentylmethylpyridine, b.p. 231° [picrate, m.p. 134–135°; platinichloride, m.p. 184° (decomp.)], is obtained. 2 mols. of EtBr give 4-n-propyl- and 4- α -ethyl-n-propyl-pyridine, b.p. 200–202° (picrate, m.p. 105°).

IV. Condensation of picoline and lepidine with $\text{Cl}[\text{CH}_2]_2\text{NEt}_2$ and NaNH_2 gives 2- γ -diethylaminopropylpyridine, b.p. 142°/24 mm. [dipicrate, m.p. 151°; platinichloride, m.p. 206–208° (decomp.)], and 4- γ -diethylaminopropylquinoline, b.p. 182°/3.5 mm. [picrate, m.p. 138°; dipicrate, m.p. 192° (decomp.)]. With α -picoline ($\text{CH}_2\text{Cl}\cdot\text{CH}_2$)₂O loses HCl, but some 2- γ -ethoxypropylpyridine, b.p. 230° (picrate, m.p. 80–81°), is formed; however, 4- γ -ethoxypropyl-, b.p. 242° (picrate, m.p. 61–62°), and 4- γ -ethoxy- α - β -ethoxyethylpropylpyridine (picrate) are formed smoothly. β -Collidine gives 3-ethyl-4- γ -ethoxypropylpyridine, b.p. 265° (picrate, m.p. 75°), and a base (picrate), m.p. 92°. $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OEt})_2$ yields 4- $\gamma\gamma$ -diethoxypropylpyridine, b.p. 153°/12 mm. (picrate, m.p. 95°). CH_2Cl_2 and $(\text{CH}_2\text{Cl})_2$ do not react with α -picoline, but $\text{CHCl}\cdot\text{CCl}_2$

yields 2- $\beta\gamma$ -dichloroallylpyridine, an oil, which rapidly polymerises, especially when heated. R. S. C.

Condensation of dihydroresorcinol with benzylideneacetophenone. B. M. MICHALOV (J. Gen. Chem. Russ., 1937, 7, 2950–2953).—cycloHexane-2 : 6-dione and $\text{CHPh}\cdot\text{CHBz}$ in piperidine (18 hr. at 100°) yield 1-(β -benzoyl- α -phenylethyl)cyclohexane-2 : 6-dione, m.p. 159–160° [monoxime, m.p. 200.5–202.5° (decomp.)]; monosemicarbazone, m.p. 220.5–221.5°, which with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in EtOH (4 hr. at the b.p.) yields the oxime, m.p. 216.5–217°, of 5-keto-2 : 4-diphenyl-5 : 6 : 7 : 8-tetrahydroquinoline, which is obtained in two isomeric forms, m.p. 111–112° and 138.5–139.5°, by hydrolysis of the oxime with 25% H_2SO_4 (2 hr. at 100°). R. T.

Nitrogen compounds in petroleum distillates. XI. Isolation of 2 : 3-dimethyl-8-ethylquinoline from the kerosene distillate of California petroleum. C. L. KEY and J. R. BAILEY (J. Amer. Chem. Soc., 1938, 60, 763–765; A., 1938, II, 29).—From the fraction, b.p. 285°, of this distillate, by way of the hydrochloride, picrate, and nitrate, is isolated 2 : 3-dimethyl-8-ethylquinoline, b.p. 284.6°/755 mm., m.p. 36.5° [picrate, m.p. 220° (decomp.)]; nitrate, m.p. 166°; hydrochloride, m.p. 212–214° (decomp.); H sulphate, m.p. 239–240°; mercurichloride, m.p. 212–214°; chromate, decomp. about 100°. This is also obtained from $o\text{-C}_6\text{H}_4\text{Et}\cdot\text{NH}_2$, tiglaldehyde, and HCl at 100°, is oxidised by CrO_3 to 2 : 3-dimethylquinoline-8-carboxylic acid (decarboxylated by soda-lime to 2 : 3-dimethylquinoline), and is converted by CH_2O at 100° into 3-methyl-8-ethyl-2- $\beta\beta'$ -dihydroxyisopropylquinoline, m.p. 94–95° (picrate, m.p. 165.5°), which with HNO_3 gives 3-methyl-8-ethylquinoline-2-carboxylic acid, m.p. 84–85°, and thence 3-methyl-8-ethylquinoline, b.p. 263° (decomp.)/746 mm. (picrate) [also obtained in 8% yield from $o\text{-C}_6\text{H}_4\text{Et}\cdot\text{NH}_2$, EtCHO, $\text{CH}_2(\text{OMe})_2$, and HCl]. R. S. C.

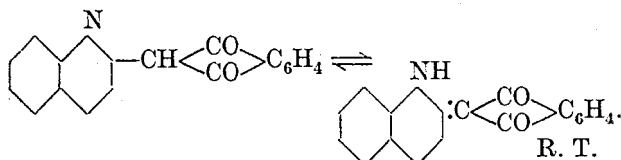
Quinoline derivatives.—See B., 1938, 486.

Direct introduction of the amino-group into the aromatic and heterocyclic nucleus. III. Action of the alkali amides on quinoline and isoquinoline. F. W. BERGSTROM (J. Org. Chem., 1938, 2, 411–430; cf. A., 1935, 223).—Quinoline (I) in liquid NH_3 dissolves 1 mol. of NaNH_2 with formation of a loose mol. compound; this gradually changes into $o\text{-C}_6\text{H}_4\text{CH}=\text{CH}\text{NNa}\cdot\text{CH}\cdot\text{NH}_2$ and $o\text{-C}_6\text{H}_4\text{CH}(\text{NH}_2)\text{CH}\text{NNa}\cdot\text{CH}$, so that decreasing amounts of (I) are recovered by treating with NH_4Cl when the solution is kept. 50% of 2- (II) and some 4-aminoquinoline (III) are obtained from (I), an excess of KNH_2 , and KNO_3 , KNO_2 being also formed; up to about 25% of (II) is obtained when KNO_3 is added to aged solutions of (I) and KNH_2 in NH_3 . NH_2 -derivatives are obtained only in presence of excess of NH_2 . Other oxidising agents or bases are ineffective. isoQuinoline and KNH_2 in NH_3 give a good yield of 1-aminoisoquinoline (IV) and 80% of H_2 ; in presence of KNO_3 only 55% of H_2 is formed; a little (IV), but no H_2 , is obtained by NaNH_2 or <1 mol. of KNH_2 and KNO_3 in NH_3 . 2-Phenylquinoline, KNH_2 , and KNO_3 give 92% of the 4- NH_2 -derivative, smaller yields being obtained even if an

excess of phenylquinoline is used. Interaction of (I) and KNH_2 in presence of Hg gives 1 K as K-Hg; in other reactions nearly 2 K are liberated. The effect of Hg in general varies from case to case. $\text{Ba}(\text{NH}_2)_2$ and (I) give (II), but no (III). An ionic mechanism is also discussed.

R. S. C.

Structure of quinophthalone. A. E. PORAI-KOSCHITZ, B. A. PORAI-KOSCHITZ, and S. A. LUIK (J. Gen. Chem. Russ., 1938, 8, 120—123).—2-Aminoquinoline in PhCl and $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ (1 hr. at 60—80°) yield 2-quinolylphthalamic acid, m.p. 187—188°, which when heated at 205—210° for 4 hr. gives N-2-quinolylphthalimide, m.p. 237—238°, +EtOH, m.p. 138—139°. N-2-Pyridylphthalimide, m.p. 228°, is prepared analogously. These compounds are colourless; it is concluded, on the grounds of their structural similarity to quinophthalone, that this has the structure



Acridine. XVIII. Nitration of acridine. β -, 4-, and 2-Nitroacridine. K. LEHMSTEDT (Ber., 1938, 71, [B], 808—814; cf. A., 1937, ii, 389).—Addition of 98% HNO_3 to acridine in conc. H_2SO_4 at 50—55° and heating of the mixture at 90—95° gives small amounts of 1- and 3-nitroacridone, large quantities of 3-nitroacridine, m.p. 215.5°, small amounts of 1-nitroacridine, m.p. 167°, 4- (I), m.p. 154°, and 2- (II), m.p. 125—127°, -nitroacridine. The isolation of (I) can be facilitated owing to its relative resistance to oxidation by CrO_3 . (I) is reduced by SnCl_2 and conc. HCl to 4-aminoacridine, m.p. 165—170° (darkening) (hydrochloride, decomp. 286° when brought into a bath preheated at 240°; picrate). 4-Acetamidoacridine, m.p. 225—226°, gives an orange NO_2 -derivative. 3-Acetamidoacridine, m.p. 230°, does not give homogeneous products when nitrated. 2:4-(NO_2) $_2\text{C}_6\text{H}_3\text{CHO}$ is reduced (TiCl_3) to 4:2- $\text{NO}_2\text{C}_6\text{H}_3(\text{NH}_2)\text{CHO}$, converted by successive treatments with PhBr, Na_2CO_3 , and Cu powder in boiling PhNO₂ and conc. H_2SO_4 into (II). H. W.

4-Aminoacridine-1-carboxylic acid. K. MATSUMURA (J. Amer. Chem. Soc., 1938, 60, 591—593).—5-Nitrodiphenylamine-2:2'-dicarboxylic acid, m.p. 324—325° (decomp.), prepared from 4:2- $\text{NO}_2\text{C}_6\text{H}_3\text{ClCO}_2\text{H}$, $o\text{-NH}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$, K_2CO_3 , and Cu in $\text{C}_5\text{H}_{11}\text{OH}$ at 160°, is converted by PCl_5 into the chloride and thence with or without AlCl_3 into 4-nitroacridone-1-carboxylic acid, m.p. 333° (decomp.) [chloride, m.p. 299° (decomp.)]. This is reduced by SnCl_2 to 4-aminoacridone-1-carboxylic acid, m.p. 289—290°, which with HCl-AcOH affords CO_2 and 4-aminoacridone (I), m.p. 289—290° (uncorr.), 299—300° (corr.), and with Na-Hg- Na_2CO_3 yields 4-aminoacridine-1-carboxylic acid, m.p. 273—274° (decomp.; sinters at 268°) (hydrochloride, decomp. 245—250°). Aminoacridones are identified by their solubilities and fluorescence. As prepared by Ullmann's method, (I) contains some of the 2-isomeride.

R. S. C.

Sulphonation of 2-nitroacridone. K. MATSUMURA (J. Amer. Chem. Soc., 1938, 60, 593—595).—2-Nitroacridone and 20% oleum at room temp. give 2-nitroacridone-7-sulphonic acid (I), m.p. 325—352° [Na , Na_2 , and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, m.p. 318—320° (decomp.)], salts; amide, m.p. >360°; Me ester, m.p. indefinite], which with PCl_5 in PhMe gives the chloride (II), m.p. 289° (decomp.). 4:2- $\text{NO}_2\text{C}_6\text{H}_3\text{ClCO}_2\text{H}$, $p\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$, Cu, and K_2CO_3 in H_2O at 115—120° give 5-nitro-2-carboxydiphenylamine-4'-sulphonic acid, m.p. 176—177° (decomp.) [Na , +0.5 H_2O , m.p. 291—292° (decomp.)], and Ba , +1.5 H_2O , m.p. >360°, salts], which with POCl_3 affords (II), hydrolysed by H_2O at 130° to (I), which is further obtained from 5-nitrodiphenylamine-2-carboxylic acid and oleum. Reduction of (I) by SnCl_2 gives 2-aminoacridone-7-sulphonic acid (III), m.p. >360°, converted into the hydrazino acid, m.p. 350° (decomp.), and thence into acridone-3-sulphonic acid. Na-Hg converts (III) into 2-aminoacridine-7-sulphonic acid (IV), m.p. >360° (Na salt), which with $\text{CH}_2\text{ClCO}_2\text{H}$ gives 2-carboxymethylaminoacridine-7-sulphonic acid, m.p. 345—360°. $p\text{-NH}_2\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ and CH_2ClCOCl give p-chloroacetamidophenylarsinic acid, m.p. 295—296° (decomp.), which with (IV) yields 7-sulpho-2-acridinylaminoacet-p-arsinoanilide, m.p. 340—360°. R. S. C.

Medicinal products from acridine compounds.
IV. Effect of changing substituents in positions 3 and 8, or of changing the amine in the side-chain, on the antimalarial activity. O. J. MAGIDSON, A. M. GRIGOROVSKI, and E. P. GALPERIN (J. Gen. Chem. Russ., 1938, 8, 56—66).—2:4-Dichloro-5-nitrobenzoic acid, p-anisidine, and K_2CO_3 and KOAc with Cu catalyst in BuOH are heated at the b.p. for 4 hr., to yield 4-chloro-5-nitro-N-p-anisylanthranilic acid, m.p. 223—224°, which, when heated for 3 hr. at the b.p. with POCl_3 , affords 5:8-dichloro-7-nitro-3-methoxyacridine, m.p. 208—210°. This condenses with $\text{NH}_2\text{CHMe}[\text{CH}_2]_3\text{NEt}_2$ (I) or with $\text{NH}_2[\text{CH}_2]_3\text{NEt}_2$ in PhOH (4 hr. at 95—100°) to 8-chloro-7-nitro-5-8-diethylamino- α -methylbutylamino-3-methoxyacridine dihydrochloride, +2 H_2O , m.p. 216—218° (chemotherapeutic index C.I. = 6.6), or 8-chloro-7-nitro-5- γ -diethylaminopropylamino-3-methoxyacridine, m.p. 136—138° (hydrochloride, m.p. 198—200°). 2:4-Dichlorobenzoic acid, heated for 3 hr. under reflux with $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, K_2CO_3 , and Cu in BuOH, gives 4-chloro-N-p-chlorophenylanthranilic acid, converted by boiling with POCl_3 into 3:5:8-trichloroacridine, m.p. 201—203°, which with (I) in PhOH gives 3:8-dichloro-5-8-diethylamino- α -methylbutylaminoacridine dihydrochloride, +2 H_2O , m.p. 220°. 5:8-Dichloro-3-methoxyacridine (II) and morpholine in PhOH (3.5 hr. at 100°) yield 8-chloro-3-methoxy-5-N-morpholinopropylaminoacridine, m.p. 222—224° (hydrochloride, m.p. 254—255°). γ -Chloropropylphthalimide and morpholine in xylene (7 hr. at the b.p.) give γ -N-morpholinopropylamine, b.p. 214—215°, condensed with (II) to give 8-chloro-5- γ -N-morpholinopropylamino-3-methoxyacridine, m.p. 142—144° (hydrochloride, +2 H_2O , m.p. 250°). 5-Chloro-8-bromo-3-methoxyacridine and (I) give 8-bromo-5-8-diethylamino- α -methylbutylamino-3-methoxyacridine,

+2H₂O, m.p. 85—87° [*dihydrochloride*, +2H₂O, m.p. 227—229° (C.I. = 7.5)]. NHMe₂ and Me γ -bromopropyl ketone at 0° yield α -dimethylaminopentan-8-one, b.p. 168—170°, the *oxime*, b.p. 138—140°/20 mm., m.p. 55—56°, of which is reduced by Na in PhMe-BuOH to δ -dimethylamino- α -methylbutylamine, b.p. 167—172°; this condenses with (II) to 8-chloro-5- δ -dimethylamino- α -methylbutylamino-3-methoxyacridine *dihydrochloride*, +3.5H₂O, m.p. 258—260° (decomp.) (C.I. = 14). 8-Chloro-3-benzoyloxyacridone in PhCl and POCl₃ (2 hr. at the b.p.) yield 5 : 8-dichloro-3-benzoyloxyacridine, m.p. 196—197°, which with (I) gives 8-chloro-5- δ -diethylamino- α -methylbutylamino-3-hydroxyacridine, an oil [*dioxalate*, +6H₂O, m.p. 157—161° (decomp.); C.I. = 3]. The C.I. is lowered by introducing an electronegative substituent into position 7, when 8 is occupied by an electropositive substituent, and also by changing the 3-OMe to OH. The activity is not affected by substituting NMe₂ for NEt₂ in the side-chain, or by substituting Cl for 3-OMe. R. T.

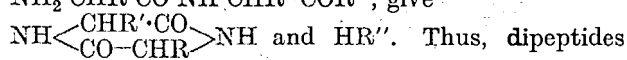
Benzacridones.—See B., 1938, 491.

Compounds of creatinine with alkali hydroxides. A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1938, 71, 40—44; cf. A., 1938, II, 77).—1 mol. of creatinine and 1.5 mols. of Na, K, or Rb hydroxides in EtOH yield mol. compounds: C₄H₇ON₃, MOH, H₂O, M = Na, turning yellow at 140° and black at 190°; K, +2H₂O, m.p. 89°, and Rb, +2H₂O, m.p. 60° (+EtOH, m.p. 35°). The Na and K compounds lose H₂O when heated in a vac. and yield alkali-creatinine compounds, readily rehydrated. A. T. P.

Picric acid compounds of creatinine. A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1938, 71, 60—67).—A mixture of equimol. solutions of creatinine-NaOH and picric acid appears to afford creatinine and Na picrate. Addition to this of 1, 2, 2.5—3.5, and 4—8 mols. of NaOH gives successively four additive compounds: C₄H₇ON₃, C₆H₃O₇N₃, 2NaOH, 2H₂O (A), dehydrated under reduced pressure at 120°; 2A, NaOH; A, NaOH; and 2A, 3NaOH, respectively; the last-named is a probable factor in Jaffe's test. A. T. P.

Action of mercuric acetate on peptides, diketopiperazines, and proteins. E. J. MATSON, W. O. TEETERS, and R. L. SHRINER (J. Org. Chem., 1938, 2, 403—410).—2 : 5-Diketopiperazine (modified prep.) with an excess of Hg(OAc)₂ in 0.5% AcOH gives the 1 : 4-(HgOAc)₂-derivative, decomp. 390—400° (block), which with an equiv. of HCl gives the (HgCl)₂-derivative, m.p. 385—395° (decomp.). With smaller amounts of Hg(OAc)₂ mixtures of HgOAc- and (HgOAc)₂-derivatives are formed. 2 : 5-Diketo-3 : 6-dimethyldiketopiperazine (modified prep.) gives similarly the 1 : 4-(HgOAc)₂-derivative, decomp. 390—400° (block). These Hg compounds are insol., with NaOH give HgO, and with (NH₄)₂S give HgS. Glycylglycine, however, is hydrolysed and oxidised with liberation of Hg. Casein, gelatin, and silk fibroin react only slowly. Casein gives a ppt. containing Hg and casein; gelatin and silk fibroin give mainly Hg. These proteins thus probably do not contain diketopiperazine groups. R. S. C.

Behaviour of peptides when heated in β -naphthol. N. LICHTENSTEIN [with S. HESTRIN, E. DIMANT, and H. BRZOZA] (J. Amer. Chem. Soc., 1938, 60, 560—563).—When heated in β -C₁₀H₇·OH (5 pts.) at 135—150° polypeptides, NH₂·CHR·CO·NH·CHR'·COR'', give

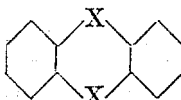


(6 examples) give only diketopiperazines; tripeptides (6 examples) give diketopiperazines with the free NH₂-acids from the terminal acid unit; a tetrapeptide, *dl*-leucylidiglycyl-*dl*-leucine, gives only the cyclic *dl*-leucylglycine anhydride, because the dipeptide liberated as HR'' undergoes self-condensation. Benzoylation of the free NH₂ prevents the reaction (4 examples), and glycylglycine, which is insol. in β -C₁₀H₇·OH, undergoes no change. Edestin and ovalbumin give mainly cryst. products, which, since they are insol. in abs. EtOH, are not simple diketopiperazines. R. S. C.

Nickel catalyst; hydrogenation of 4-amino-5-cyano-2-methylpyrimidine. M. DELÉPINE (Compt. rend., 1938, 206, 866—869).—During hydrogenation (Raney Ni in NH₃-MeOH) of 4-amino-5-cyano-2-methylpyrimidine to the corresponding 5-NH₂·CH₂ compound, a deposit is formed on the Ni, considered to be a complex (I) of Ni and the 5-CHO-derivative (II); (I) is decomposed by boiling aq. AcOH to (II), reconverted into (I) by heating with Ni^{III} salts in aq. NH₃. The mechanism of formation of (I) [(II) and NH₃ yield the 5-NH·CH derivative, converted by NiO into (I); (II) and H₂ give the 5-OH·CH₂ compound] and modifications in procedure [H₂-Ni-H₂O-MeOH-NH₃-NiCl₃·6H₂O] to prevent complex formation are recorded. A. T. P.

Pyrimidines.—See B., 1938, 489.

Configuration of heterocyclic compounds. VIII. Configuration of anthracene, 9 : 10-dihydroanthracene, phenazine, 9 : 10-dimethyl-9 : 10-dihydrophenazine, thianthren, and selenanthren. (MISS) I. G. M. CAMPBELL, (MRS.) C. G. LE FÈVRE, R. J. W. LE FÈVRE, and E. E. TURNER (J.C.S., 1938, 404—409).—Theoretical considerations show that a mol. (I) will be least strained when it is folded, provided that the atom or group X prefers a valency angle approximating to the tetrahedral angle. 9 : 10-Dihydroanthracene (X = CH₂) should be folded, and its dipole moment is not 0, but

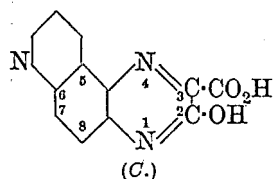


(I.)

is of the same order as that of dibenzyl. Dipole moments of anthracene, phenazine, thianthren, and selenanthren are also given, whilst that of 9 : 10-dimethyl-9 : 10-dihydrophenazine (X = NMe) could correspond with folding of the mol. about the X-X axis and a certain disposition of the N-Me bonds. The stereoisomerism of anthracene derivatives (Schlenk *et al.*, A., 1928, 1031) is discussed. F. R. S.

Phenazine series. I. Oxidation of phenazine. Z. V. PUSCHKAREVA and G. I. AGBALOVA. **II. Oxidation of monoacetyldihydrophenazine.** Z. P. PUSCHKAREVA and I. J. POSTOVSKI (J. Gen. Chem. Russ., 1938, 8, 151—157, 158—163).—I.

The pyridinoalloxazines are very stable towards alkali. In neutral solution at room temp. (I) and alloxan afford *alloxanaminoquinolyimide*, m.p. 353° (decomp.) (Na and Ag salts). Its solutions have a greenish-yellow fluorescence in ultra-violet light; this is extinguished by mineral acid or alkali hydroxide. In aq. Na_2CO_3 an intense blue-green fluorescence is visible in daylight. It is converted by the short



action of boiling NaOH into (probably) 2-hydroxypyridino-3':2'-5:6-quinoxaline-3-carboxylic acid, m.p. 320°, also obtained from (I) and $\text{CO}(\text{CO}_2\text{H})_2$ in faintly acid solution. Contrary to Kühling, the formation of alloxazines does not occur exclusively from the salts with mineral acids but also from the free base particularly if the temp. is raised. Mineral acids are not essential but helpful since they promote the exclusive formation of alloxazines without other reaction products.

H. W.

N-Aralkylmorpholines. M. T. LEFFLER and E. H. VOLWILER (J. Amer. Chem. Soc., 1938, 60, 896—899).—1-Benzylmorpholines have local anæsthetic action similar to that of procaine and are less toxic. The 4'-Br-derivative is most effective and its solution can be sterilised. Nitration of $\text{Ph}[\text{CH}_2]_3\text{Br}$ gives γ -p-nitrophenylpropyl bromide, b.p. 152—156°/2 mm. o-OBu· $\text{C}_6\text{H}_4\cdot\text{NO}_2$, $(\text{CH}_2\text{O})_3$, ZnCl_2 , and HCl in light petroleum at 85° give 3-nitro-4-butoxybenzyl chloride, b.p. 162—165°/4 mm. o-Butoxybenzyl chloride, b.p. 102—103°/4 mm., is prepared from the alcohol and anhyd. HCl at 5—10°, and 3-bromo-4-butoxybenzyl chloride, b.p. 135—140°/3 mm., from 1:3:4- $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{OBU}$ and Cl_2 in light at 170°. Condensation of the aralkyl halide with morpholine or its 2:6-Me₂ derivative yields 1-o-, b.p. 160—163°/4 mm., and -p-nitro-, m.p. 79—80°, -3'-nitro-4'-butoxy-, b.p. 162—164°/3 mm., -o- (hydrochloride, m.p. 216—217°), and -p-bromo- (I), b.p. 138—142°/4 mm., m.p. 83—84° [hydrochloride, m.p. 280° (block)], -p-chloro-, m.p. 68—69° [hydrochloride, m.p. 258° (block)], -3'-bromo-4'-butoxy-, b.p. 185—188°/3 mm. (hydrochloride, m.p. 183·5—184·5°), and -o-butoxy-benzylmorpholine (hydrochloride, m.p. 159·5—160·5°), 1-p-nitrobenzyl-, b.p. 163—165°/3 mm., m.p. 66—67°, -benzyl-, b.p. 102—104°/3 mm. (hydrochloride, m.p. 184—185°), -p-chlorobenzyl- (hydrochloride, m.p. 189—190°), and -cinnamyl-2:6-dimethylmorpholine, b.p. 140—142°/3 mm., 1- β -p-nitrophenylethyl-, b.p. 260°/740 mm., 1- γ -p-nitrophenylpropyl-, b.p. 175—178°/2 mm., 1- α - (hydrochloride, m.p. 211—212°), and - β -phenylethyl-, b.p. 107—108°/3 mm. [hydrochloride, m.p. 238° (block)], 1- γ -phenylpropyl-, b.p. 113—115°/2 mm. (hydrochloride, m.p. 138—139°), 1-cinnamyl-, b.p. 132—134°/3 mm. [hydrochloride, m.p. 216° (block)], and 1- α -naphthylmethylmorpholine (hydrochloride, m.p. 234—235°). Reduction of the NO_2 -compounds by $\text{Fe}\cdot\text{H}_2\text{O}$ affords 1-o-, b.p. 150—152°/4 mm., and -p-amino- (II), m.p. 100·5—101·5° (hydrochloride, m.p. 188—190°), and 1-3'-amino-4'-butoxy-benzylmorpholine (hydrochloride, m.p. 199·5—200·5°), 1-p-aminophenylethyl-, m.p. 80·5—81·5°, and 1- γ -p-aminophenylpropyl-

morpholine, b.p. 156—160°/2 mm. (hydrochloride, m.p. 195—196°), and 1-p-aminobenzyl-2:6-dimethylmorpholine, b.p. 160—162°/2 mm. [hydrochloride, m.p. 214° (block)]. Passage of Br-air through (I) in H_2O gives 2:4:6- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NH}_2$, but Br-AcOH yields 1-3':5'-dibromo-4'-aminobenzylmorpholine, m.p. 62—63° (hydrochloride, m.p. 260°). With BuBr at 50—90° (II) gives 1-p-n-butylaminobenzylmorpholine (hydrochloride, m.p. 180—182°). With $\text{H}_2\text{SO}_4\text{--HNO}_3$ (I) gives an oily NO_2 -derivative, reduced to 1-4'-bromo-3'-aminobenzylmorpholine, m.p. 102—103°. R. S. C.

Derivatives of 6:7-dimethoxybenzoparathiazine. K. J. BALDICK and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 112—117).—4:5-Dimethoxy-thiophenol and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ in 25% aq. NaOH at 50° afford the -phenylthioglycollic acid (I), m.p. 106°, which with HNO_3 (d 1·42) in AcOH at 20° gives the 2- NO_2 -derivative (II), m.p. 222°, converted by Sn-HCl into 3-ketodihydro-6:7-dimethoxybenz-1:4-thiazine (III), m.p. 186—187°. (I) and HNO_3 (d 1·4) in AcOH at 100° or (II) and 3% H_2O_2 in boiling AcOH give 2-nitro-4:5-dimethoxyphenylsulphinylacetic acid, m.p. 203°, oxidised, as also is (II), with KMnO_4 in aq. MgSO_4 at 10—15° to the -sulphonylacetic acid, m.p. 200°, which with Sn-HCl yields 3-ketodihydro-6:7-dimethoxybenzoparasulphazone [2-oximino-3-keto-6:7-dimethoxy-2:3-dihydrobenz-1:4-thiazine 1:1-dioxide] (IV) (+ H_2O , removed at 110° in a vac. with P_2O_5), m.p. 233—234° [NO-derivative, decomp. 195—200°; 2-(azo- α -naphthalene-5-sodium sulphonate) derivative]. (HI) and (IV) do not condense with acenaphthenequinone; (IV) did not react with PhCHO. A. T. P.

Reactions of methylene-blue with metallic salts. II. R. RALEA (Ann. Sci. Univ. Jassy, 1938, 24, 157—162).—Interaction of $2\text{RCl}\cdot\text{CdI}_2$ ($\text{R} = \text{C}_6\text{H}_{13}\text{N}_3\text{S}$) with HgCl_2 in boiling H_2O gives the salt, $2\text{RCl}\cdot\text{HgI}$, transformed by aq. $\text{K}_2\text{S}_2\text{O}_8$ into the compound, $\text{R}_2\text{S}_2\text{O}_8\cdot\text{HgI}_2$. Methylene-blue (I) is converted by $\text{K}_3\text{Co}(\text{CN})_6$ and $\text{K}_3\text{Co}(\text{NO}_2)_6$, respectively, into the substances $\text{R}_3\text{Co}(\text{CN})_6$ and $\text{R}_3\text{Co}(\text{NO}_2)_6$. Excess of $\text{K}_2\text{Cd}(\text{CN})_4$ and (I) afford the salt, $\text{R}_2\text{Cd}(\text{CN})_4$, whilst NH_4CNS and $2\text{RCl}\cdot\text{CdCl}_2$ yield the compound, $\text{R}_2\text{Cd}(\text{SCN})_4$. $\text{R}\cdot\text{CNS}$ and CdCl_2 or CdBr_2 respectively yield the substances, $2\text{RCl}\cdot\text{CdCl}_2$ (II) and $2\text{RCl}\cdot\text{CdBr}_2$, which differ somewhat from those derived directly from the components. An excess of boiling aq. KI converts (H) into the substance, $2\text{RI}\cdot\text{CdCl}_2$, transformed by HgCl_2 into the product, $\text{RI}_2\cdot\text{HgCl}_2$, which is unchanged by $\text{K}_2\text{S}_2\text{O}_8$. Treatment of (H) with an equiv. of aq. KI gives the isomeric salt, $2\text{RCl}\cdot\text{CdI}_2$, which with HgCl_2 affords a green product, transformed by $\text{K}_2\text{S}_2\text{O}_8$ into the salt, $\text{R}_2\text{S}_2\text{O}_8\cdot\text{HgI}_2$. The constitution of the additive compounds is uncertain. H. W.

Cytisine. VI. Synthesis of 8-keto-2:4-dimethyl- β -quinolizine, a degradation product of cytisine. E. SPÄTH and F. GALINOVSKY (Ber., 1938, 71, [B], 721—724; cf. A., 1936, 741).—Et 3:5-dimethylpicolinate (I), b.p. 90—100° (bath)/0·01 mm. (picrate, m.p. 111—112°), condenses with Et₂ succinate and EtOH-free NaOEt in C_6H_6 to Et β -3:5-dimethyl-2-pyridoylpropionate, m.p. 68—69°, reduced (Clemmensen) to Et γ -3:5-dimethyl-2-pyridylbutyrate, b.p.

90° (bath)/0.01 mm., which is hydrolysed and then hydrogenated (PtO₂) to γ -3:5-dimethyl-2-piperidyl-butyric acid hydrochloride, m.p. 194—196° (vac.). This is esterified and then heated at 200°, whereby 8-keto-2:4-dimethyloctahydroquinolizine (II), b.p. 160° (bath)/10 mm., is obtained. Dehydrogenation of (II) by Pd-sponge at 270—280° gives 3:5-dimethyl-2-propylpyridine (III) and 8-keto-2:4-dimethyl- ψ -quinolizine, identical with the degradation product from cytisine. Condensation of (I) with EtCO₂Et and EtOH-free NaOEt in C₆H₆ yields 3:5-dimethyl-2-pyridyl Et ketone, b.p. 120° (bath)/10 mm., m.p. 45—46°, reduced (Zn—Hg and Sn—HCl) to some (III) with a larger proportion of 3:5-dimethyl-2-pyridyl-ethylcarbinol, b.p. 110—120° (bath)/10 mm. (picrate, m.p. 116—117°). The latter is transformed by P₂O₅ in boiling PhMe into 3:5-dimethyl-2-propenylpyridine, b.p. 90—100°/10 mm. [picrate, m.p. 179—180° (vac.)], hydrogenated (Pd-sponge in AcOH) to (III).

H. W.

Syntheses of new antimalarials. III. Lupinine derivatives. I. L. KNUNIANZ and Z. V. BENEVOLENSKAJA (J. Gen. Chem. Russ., 1937, 7, 2930—2933).—8-Amino-6-methoxyquinoline and chlorolupinan (I) (8 hr. at 170—180°) yield 8-lupinylamino-6-methoxyquinoline (II), b.p. 242—245°/2 mm. (trihydrochloride, +5H₂O, m.p. 140—142°). (I) and 3-amino-5-methoxy-1-methylbenzthiazole (10 hr. at 180—190°) afford 3-lupinylamino-5-methoxy-1-methylbenzthiazole (III), b.p. 250—260°/3 mm. (dihydrochloride, m.p. 216—218°). 5:7-Dichloro-3-methoxyacridine in PhOH and aminolupinan (2 hr. at 100°) yield 7-chloro-5-lupinylamino-3-methoxyacridine (IV), m.p. 140° [dihydrochloride, +3H₂O, m.p. 283° (decomp.)]. (II) and (IV), but not (III), are powerful antimalarials.

R. T.

Alkaloid from *Dephinium brownii*, Rydb. R. H. F. MANSKE (Canad. J. Res., 1938, 16, B, 57—60).—Extraction of the dried aerial portion of the plant with MeOH leads to the isolation of about 0.5% of a non-cryst. alkaloid (I) which does not give cryst. salts with HCl, H₂SO₄, AcOH, H₂C₂O₄, citric acid, HClO₄, or H₃PO₄. Hydrolysis of (I) by KOH yields a cryst. base, C₂₀H₃₇O₇N or C₂₃H₃₃O₇N (possibly C₂₀H₃₃O₆N), m.p. 120—121° after considerable softening, [α]_D²⁵ +52.2° in MeOH, in which 3 or 4 OMe are probably present. Mannitol, o-NH₂-C₆H₄-CO₂H, and methylsuccinic acid are also identified.

H. W.

Electrolytic reduction of morphine and codeine. S. TAKAGI and T. UEDA (J. Pharm. Soc. Japan, 1936, 56, 44—53).—Electrolysis with morphine dissolved in 10% HCl in a divided cell as catholyte (Pt cathode) and 10% H₂SO₄ as anolyte (Pd anode) gave an 89% yield of dihydromorphine hydrochloride at a c.d. of 4 amp. per sq. dm. Reduction of codeinephosphoric acid under similar conditions gave a 97% yield of dihydrocodeinephosphoric acid at c.d. 4 amp. per sq. dm.

CH. ABS. (e)

Hofmann degradation of domesticine ethers. H. SHISHIDO (Bull. Chem. Soc. Japan, 1938, 13, 247—252).—The structure of domesticine is confirmed by the identity of the degradation products of its ethers with those of synthetic ethers. Natural *d*-domesticine

Me ether gives a methiodide, m.p. 105—107°, decomp. 117°, converted by KOH into the methine [*de-N-Me* base], m.p. 133—134°, the methiodide, m.p. 294—295° (decomp.), of which gives the methochloride and thence, by 10% KOH—NMe₃, 3:4-dimethoxy-6:7-methylenedioxy-1-vinylphenanthrene (I), m.p. 142—143°, and a (?) polymeride, m.p. about 250—270° (decomp.). KMnO₄ oxidises (I) to 3:4-dimethoxy-6:7-methylenedioxyphenanthrene-1-carboxylic acid, m.p. 252—253° (Me ester, m.p. 148—150°), decarboxylated by Cu in boiling quinoline to 5:6-dimethoxy-2:3-methylenedioxyphenanthrene, m.p. 127—128.5°. Synthetic *dl*-domesticine Me ether methiodide, m.p. 230—232°, gives the same degradation products. *dl*-Domesticine Et ether methiodide, m.p. 225—227° (decomp.), gives the methine [*de-N-Me* base], m.p. 133—134.5°, the methiodide, m.p. 290—291° (decomp.), of which affords 3-methoxy-4-ethoxy-6:7-methylenedioxy-1-vinylphenanthrene, m.p. 114—115.5° [with NMe₃ and a polymeride, m.p. 250—260° (decomp.)], 3-methoxy-4-ethoxy-6:7-methylenedioxyphenanthrene-1-carboxylic acid, m.p. 243—245°, and 6-methoxy-5-ethoxy-2:3-methylenedioxyphenanthrene, m.p. 134—135°. The *d*-Et ether affords the same products. *dl*-isoDomesticine Et ether methiodide, m.p. 224—226° (decomp.), affords the methine [*de-N-Me* base], m.p. 117—118° [*H* oxalate, m.p. 195—197° (decomp.)], the methiodide, m.p. 289—290° (decomp.), thereof, 4-methoxy-3-ethoxy-6:7-methylenedioxy-1-vinylphenanthrene, m.p. 119—120.5° [with NMe₃ and a polymeride, m.p. 240—250° (decomp.)], 4-methoxy-3-ethoxy-6:7-methylenedioxyphenanthrene-1-carboxylic acid, m.p. 235—236.5° [with a neutral substance, m.p. 280—282° (decomp.)], and 5-methoxy-6-ethoxy-2:3-methylenedioxyphenanthrene, m.p. 126—128°.

R. S. C.

Amides of *p*-arsonophenylacetic acid. E. WALTON (J.C.S., 1938, 471—472).—Me *p*-arsonophenylacetate [*Na* salt (+H₂O)], from the corresponding acid, with the appropriate amine gives phenylacetamide- (*NH*₄ salt), phenylacetate-methyl- [*Na* salt (+H₂O)], -dimethyl- (*Na* salt), -ethyl- (*Na* salt), -*n*-propylamide- (*Na* and *n*-propylamine salts), and -piperidide- (*Na* salt), and phenylacetanilide-*p*-arsinic acid (*Na*₂ salt). The *Na* salts show trypanocidal activity.

F. R. S.

Constitution and action of aromatic arsinic acids. I. K. BURSCHKIES and M. ROTHERMUNDT (Arch. Pharm., 1938, 276, 226—234).—The therapeutic activity of 4-amino- and 4-amino-2-hydroxyphenylarsinic acid is lessened by the introduction of higher acid residues of the homologous acyl series. The following compounds are prepared from the requisite arsinic acid, 2*N*-NaOH, and the required acid anhydride: 4-*n*-propionamido-, m.p. 232—233° (decomp.); 4-*n*-valeramido-, m.p. 227—228°; 4-isovaleramido-, m.p. 232°; 2-hydroxyphenylarsinic acid; 3-dipropionamido-, m.p. 182°; 3-isobutyramido-, m.p. 194—195°; 3-*n*-valeramido-, m.p. 208—209°; 3-isovaleramido-, m.p. 226—227°; 4-hydroxyphenylarsinic acid. 4-Carbethoxyamido-2-hydroxyphenylarsinic acid, m.p. 220—221°, is transformed by conc. H₂SO₄ and HNO₃ (*d* 1.52) at —5° into 3-nitro-4-carbethoxyamido-2-hydroxyphenylarsinic acid, decomp. 240°, reduced by Na₂S₂O₄ to 3-amino-4-carbethoxy-

amido-2-hydroxyphenylarsinic acid, decomp. 170°. 3-Carboethoxyamido-4-hydroxyphenylarsinic acid has m.p. 210—211°. 3-Acetamido-4-hydroxyphenylarsinic acid is nitrated [conc. H_2SO_4 and HNO_3 (d 1.52) at -10°] to 5-nitro-3-acetamido-4-hydroxyphenylarsinic acid, m.p. 218—220°, reduced to 5-amino-3-acetamido-4-hydroxyphenylarsinic acid. 4-o-Hydroxybenzylideneamino-2-hydroxyphenylarsinic acid decomposes at 210°. H. W.

Derivatives of *p*-arsanilic acid. VIII. *p*-Arsono-oxanilic and *p*-arsonohexadecanedicarboxylanilic acids and related compounds. (Sir) G. MORGAN and E. WALTON (J.C.S., 1938, 442—444).—*Me p*-arsono-oxanilate, from the corresponding acid (*Et* ester, dimorphous), with conc. aq. NH_3 gives oxanilamide-*p*-arsinic acid (*Na* salt), and with the appropriate amine yields oxanilo-methyl- [*Na* salt (+2 H_2O)], -dimethyl- [*Na* salt (+ H_2O)], -ethyl- [*Na* salt (+ H_2O)], and -*n*-propyl-amide- (*Na* salt), and -piperidide-*p*-arsinic acid [*Na* salt (+ H_2O)], and oxanilide-*p*-arsinic acid [*Na* salt (+ H_2O)]. *p*-Arsono-oxanilic acid forms three NH_4Ph salts, corresponding with acid : base, 1 : 2, 1 : 1, and 2 : 1. The trypanocidal activity of this series is more or less true to type, whilst their toxicity is greater. Hexadecanedicarboxylic acid and SOCl_2 , followed by *Na p*-arsanilate, give *p*-arsono-hexadecanedicarboxylanilic acid (*Na* salt) and hexadecanedicarboxylanilide-*pp'*-diarsinic acid. *Me* hexadecane- $\alpha\omega$ -dicarboxylate and KOH afford *Me H* hexadecane- $\alpha\omega$ -dicarboxylate, m.p. 72—74°, which with SOCl_2 yields the acid chloride, not convertible into the *Me* ester. The free acid with MeOH and H_2SO_4 (trace) gives crude *Me p*-arsono-hexadecanedicarboxylanilate. F. R. S.

Arsenicals containing the furan nucleus. III. β -Substituted furan arsenicals. H. W. BECK and C. S. HAMILTON (J. Amer. Chem. Soc., 1938, 60, 620—621; cf. A., 1936, 217).—3-Chloromercurifuran and AsCl_3 (0.33 mol.) in C_6H_6 give 36% of tri-3-furylarsine, an oil, and 28% of the HgCl_2 additive compound, m.p. 152—153°, thereof, the latter product being obtained in 70% yield by AsCl_3 (1 mol.) in EtOH . *Me* 5-bromo-4-chloromercuri-2-furoate (prep. by way of the *OAc*-derivative, m.p. 198—199°), m.p. 238°, does not react with AsCl_3 , but with AsBr_3 gives 5-bromo-2-carbomethoxy-4-furyldibromoarsine (I), m.p. 95—96°. *Et* 5-bromo-4-acetoxy-, m.p. 188—189°, and -4-chloro-mercuri-2-furoate, m.p. 162°, and 5-bromo-2-carboethoxy-4-furyldibromoarsine, m.p. 52—53°, are similarly obtained from *Et* 5-bromo-2-furoate. The *As*-*C* linking of (I) resists HgCl_2 or *I*, but long heating with H_2O gives *Me* 5-bromo-2-furoate. 3-Furylarsines are more stable than the 2-analogues. R. S. C.

Constitution of organo-magnesium solutions. T. R. BEYER (Kimya Annali, 1937, 2, No. 14, 16—22; No. 15, 18—34).—I. A review of the literature.—II. A new theory postulates the presence of α - and β -etherates, $(\text{RMgX})_2[\text{OEt}_2]_2$, the relative proportions depending on *R*. The mechanism of the reaction with aldehydes and esters is formulated. The etherates differ from each other in the disposition of valencies. F. R. S.

Reactions between mercury diaryls and selenium tetrabromide. H. M. LEICESTER (J. Amer. Chem. Soc., 1938, 60, 619—620).— HgPh_2 , $\text{Hg}(\text{C}_6\text{H}_4\text{Me}-p)_2$, $\text{Hg}(\text{C}_{10}\text{H}_7-\beta)_2$, and $\text{Hg}(\text{C}_6\text{H}_4\text{Ph})_2$ with SeBr_4 (0.33 mol.) give excellent yields of diaryl-selenides, aryl bromide, and *Hg* aryl bromide. With more SeBr_4 further change occurs thus: $\text{SeBr}_4 + 3\text{HgArBr} \rightarrow \text{Ar}_2\text{Se} + \text{ArBr} + 3\text{HgBr}_2$, a reaction realised separately with HgPhBr . R. S. C.

Reaction of tin and of tin-sodium alloy with mercury- and tin-organic salts, with the object of synthesising highly arylated tin-organic compounds. M. M. NADJ and K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1938, 8, 42—50).—Compounds of the type SnR_4 and SnR_3Cl are obtained in good yield by the reactions $6\text{HgRCl} + 3\text{Sn} + 6\text{Na} \rightarrow 3\text{SnR}_2 + 6\text{NaCl} + 6\text{Hg}$; $3\text{SnR}_2 \rightarrow \text{Sn}_2\text{R}_6 + \text{Sn}$; $\text{Sn}_2\text{R}_6 \rightarrow \text{SnR}_4 + \text{SnR}_2$, or $6\text{HgRCl} + 3\text{Sn} \rightarrow 3\text{SnR}_2\text{Cl}_2 + 6\text{Hg}$; $3\text{SnR}_2\text{Cl}_2 \rightarrow 2\text{SnR}_3\text{Cl} + \text{SnCl}_4$; $\text{SnCl}_4 + \text{Sn} \rightarrow 2\text{SnCl}_2$ (*R* = *Ph*, *p*- $\text{C}_6\text{H}_4\text{Cl}$, *p*- $\text{C}_6\text{H}_4\text{Me}$, *p*- $\text{C}_6\text{H}_4\text{CO}_2\text{Et}$, and CH_2Ph). The following compounds are described: $[\text{Sn}(\text{C}_6\text{H}_4\text{CO}_2\text{Et})_3]_2\text{S}$, m.p. 132—133°, $\text{Sn}_2(\text{C}_6\text{H}_4\text{Cl}-p)_6$, m.p. 224—226°, $\text{Sn}(\text{CH}_2\text{Ph})_3\cdot\text{OH}$, m.p. 122—124°. R. T.

Tin-organic compounds of the type SnAr_2X_2 , containing a carboethoxy-group in the benzene ring. I. T. ESKIN, A. N. NESMEJANOV, and K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1938, 8, 35—41).— SnPh_2Cl_2 in EtOH and H_2S yield diphenylstannane sulphide, m.p. 183—184°. The compounds SnR_2X_2 (*R* = *p*- $\text{C}_6\text{H}_4\text{CO}_2\text{Et}$, *X* = *Cl*, m.p. 102—103°, *X* = *Br*, m.p. 69—69.5°, and *X* = *I*, an oil) are prepared by the reaction $\text{HgR}_2 + \text{SnX}_2 \rightarrow \text{Hg} + \text{SnR}_2\text{X}_2$, and the compounds SnR_2S , m.p. 141.5—142.5°, and SnR_2O , not melting at 300°, are hence prepared. SnR_2Cl_2 and MgPhBr in Et_2O give the compound $\text{SnPh}_2(\text{C}_6\text{H}_2\text{Ph}_2\cdot\text{OH})_2$, m.p. 265—266°. SnR_2I_2 and 8-hydroxyquinoline in EtOH give SnR_2Q_2 , m.p. 216—217° (*Q* = $\text{C}_9\text{H}_6\text{N}\cdot\text{O}$). R. T.

Structure of proteins. Possibility of determining the cyclic form of amino-acid anhydrides by Blanchetière's method. N. I. GAVRILOV and M. A. POLUNINA (Bull. Soc. chim., 1938, [v], 5, 454—459).—Blanchetière's method removes proline and hydroxyproline, as well as α - NH_2 -acids, almost quantitatively. Hydrolysis of gelatin by 2% H_2SO_4 at 180°/10 atm. or by 25% H_2SO_4 gives only 5.34% of diketopiperazine-*N*; a possible explanation is suggested. R. S. C.

Combination between magnesium and proteins in solution. I, II. W. DUCE (Boll. Soc. ital. Biol. sperim., 1937, 12, 793—794, 794—795).—I. Measurements of the potential of solutions of varying concn. of gelatin and $\text{Mg}(\text{OAc})_2$ indicate that, like *Ca* (Eversole *et al.*, A., 1934, 253), *Mg* combines with gelatin at p_H 7.0—7.2 at 20°.

II. Dialysis of aq. gelatin- NaCl - $\text{Mg}(\text{OAc})_2$ against aq. NaCl and subsequent determinations of Cl^- and Mg^{++} indicate that, when allowance is made for the Donnan equilibrium, *Mg* combines with gelatin at p_H 7.0—7.2 at 20°. F. O. H.

Determination of glucosamine in proteins. M. SØRENSEN (Compt. rend. Trav. Lab. Carlsberg, 1938,

22, 487—493).—The protein is hydrolysed with HCl, and the glucosamine condensed with $\text{CH}_3\text{Ac}\cdot\text{OMe}$ to form a pyrrole derivative. The red colour produced by the latter with $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ is compared with controls in a step-photometer. The % of glucosamine in the following proteins are: ovalbumin 1.4, egg-mucoid 13.6, serum-albumin 0.37, and serum-globulin 1.7. J. N. A.

Hydration and denaturation of proteins.—See A., 1938, I, 311.

Semi-micro-determination of carbon and hydrogen. B. HEPNER and M. POJAS (Compt. rend. XVII Cong. Chim. Ind., 1937, 397—399).—Ter Meulen and Heslinga's method is made applicable to compounds containing N, S, and halogens by the use of a Pt spiral and a mixed MnO_2 and Pb_3O_4 catalyst at 400° followed by K_2CrO_4 at 200° in the combustion train. The apparatus is described in detail.

F. N. W.

Risk of explosion in the use of perchloric acid. E. KAHANE (Compt. rend. XVII Cong. Chim. Ind., 1937, 471—475; cf. A., 1938, II, 76).—Precautions to be observed in the use of the $\text{HNO}_3 + \text{HClO}_4$ and the $\text{HNO}_3 + \text{H}_2\text{SO}_4 + \text{HClO}_4$ methods are (i) preliminary attack by HNO_3 , and (ii) dilution in an inert medium, i.e., a large excess of HClO_4 in the first and sufficient H_2SO_4 in the second method. The first method should not be used for $>$ a few g. of material.

L. S. T.

Mercuric selenite as catalyst in the Kjeldahl determination of nitrogen.—See A., 1938, III, 546.

Colorimetric determination of minute amounts of tin in organic matter.—See A., 1938, I, 326.

Thiocyanogen iodide number of hydrocarbons. H. P. KAUFMANN and H. GROSSE-OETRINGHAUS (Oel u. Kohle, 1938, 14, 199—201; cf. A., 1937, II, 359).—CNSI solutions in CCl_4 give better reproducibility and shorter reaction times than those in C_6H_6 . Standard 0.2N-CNSI solution is prepared as follows: 900 c.c. of CCl_4 (1:1) mixed with 100 c.c. of AcOH and Ac_2O is kept ≤ 8 days. 25 g. of $\text{Pb}(\text{CNS})_2$ and 2.8 g. of Br are added and the mixture is shaken in diffused light until decolorisation is complete. 13 g. of I are then added and when this has dissolved the solution is filtered. Pure materials must be used; a method of preparing pure $\text{Pb}(\text{CNS})_2$ is given. 0.1—0.2 g. of the hydrocarbon to be tested, mixed with 20 c.c. of the CNSI solution, is kept for 15 hr. in the dark; 50 c.c. of 100% aq. KI are then added rapidly and the liberated I is immediately titrated with $\text{Na}_2\text{S}_2\text{O}_3$. A blank is carried out. The CNSI no. gives a measure of unsaturation; practically no substitution occurs.

A. B. M.

Identification and determination of volatile alcohols and acids. T. E. FRIEDEMANN (J. Biol. Chem., 1938, 123, 161—184).—Volatile acids are separated by steam-distillation (15—20 min.) with acid $\text{Na}_2\text{WO}_4\text{--MgSO}_4$ followed by redistillation from acid $\text{MgSO}_4\text{--H}_2\text{O}$ to remove formic, pyruvic, crotonic, and lactic acids, etc. The distillate is fractionally distilled (Duclaux) from acid $\text{MgSO}_4\text{--H}_2\text{O}$, one half of each fraction being aerated to remove CO_2 and titrated with 0.01N-NaOH. The $\text{Et}_2\text{O--H}_2\text{O}$ dis-

tribution const. (K), i.e., % remaining in the aq. phase, is determined with the other half. From the rate of this distillation, K , and the titration vals., the acids are identified and may be determined if >3 are present. The following vals. for K for 1:1 $\text{H}_2\text{O--Et}_2\text{O}$ are recorded: AcOH 73.5, EtCO_2H 42.4, PrCO_2H 18.2, crotonic acid 25.6, $\text{Pr}^i\text{CO}_2\text{H}$ 16.8. HCO_2H is determined by oxidation with HgO . Alcohols are determined by distillation from $\text{Na}_2\text{WO}_4\text{--HgSO}_4$ followed by redistillation from $\text{Ca}(\text{OH})_2\text{--HgO}$, thus removing acids, NH_2 -compounds, ketones, aldehydes, and phenols. The distillate is oxidised by $2\text{N--H}_2\text{SO}_4\text{--K}_2\text{Cr}_2\text{O}_7$ followed by titration and determination of K , whence the alcohols are identified. Results for EtOH in blood and for alcohols and acids in cultures of pathogenic micro-organisms agree with those obtained by the method of Friedemann and Klaas (cf. A., 1936, 1229). EtOH is the only alcohol and AcOH the only volatile acid (not removed by HgO) produced by these organisms in carbohydrate-rich media.

E. G. B.

Determination of [ethyl] alcohol [in aqueous solutions]. A. NINNI (Suomen Kem., 1938, 11, A, 45—50).—Comparison of η for an $\text{EtOH--H}_2\text{O}$ mixture with η for H_2O gives two vals. for the EtOH concn., the correct one being found by (rough) measurement of γ . Corrections are applied to give an accuracy of 0.05%.

M. H. M. A.

Determination of ethylene glycol. R. CUTHILL and C. ATKINS (Analyst, 1938, 63, 259—261).— $(\text{CH}_2\cdot\text{OH})_2$ is quantitatively converted into CO_2 and H_2O when treated for $1\frac{1}{2}$ hr. with alkaline KMnO_4 , then acidified with H_2SO_4 , and kept for a further 1 hr. A known amount of KMnO_4 is added initially and the excess titrated iodimetrically.

E. C. S.

Determination of mono- and di-saccharides with hypiodide. K. MYRBÄCK and B. ÖRTENBLAD (Svensk Kem. Tidskr., 1938, 50, 72—77).—Glucose, galactose, arabinose, maltose, and lactose can be determined accurately by adding I followed by NaOH, and titrating the excess of I. Owing to the formation of NaIO_3 , it is necessary either to use a large excess of I or to add the NaOH very slowly (2—4 min.).

A. L.

Manometric determination of amino-acids. M. F. MASON (Biochem. J., 1938, 32, 719—724).— $\alpha\text{-NH}_2$ -acids are decarboxylated by heating with ninhydrin in H_2O , and the gasometric determination of CO_2 in the Van Slyke apparatus is less liable to error than the colorimetric method. No decarboxylation of peptides (except glutathione) and keto-hydroxy-acids occurs. The method is not satisfactory for alanine, serine, or tryptophan.

A. T.

Nephelometric determination of morphine with vanadomolybdic acid. W. DECKERT (Z. anal. Chem., 1938, 112, 241—257).—Of a large no. of alkaloids, only morphine, dilaudide, and heroin have a sensitivity to $\text{HVO}_3 + \text{H}_2\text{MoO}_4 \gg$ to H_2MoO_4 , so that when an acid solution is treated with $(\text{NH}_4)_2\text{MoO}_4$ and the filtrate treated with NH_4VO_3 the degree of turbidity is a quant. measure of the concn. of these. The morphine complex is $\text{V}(\text{OH})_5\cdot 2\text{MoO}_3\cdot \text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$. Details are given of the procedure (cf. A., 1936, 652).

F. J. G.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JULY, 1938.

Tautomerism and organic chemistry. V. V. RAZUMOVSKI (J. Gen. Chem. Russ., 1938, 8, 255—265).—Theoretical. R. T.

Transmitting mechanisms of organic reactions. E. A. SCHILOV (Compt. rend. Acad. Sci. U.R.S.S., 1938, 18, 649—653).—Theoretical. An attempt to explain the mechanism of addition and other org. reactions by the participation of a third mol. which may be an added or accidentally present catalyst, or the mol. of the solvent, or the walls of the vessel. In most cases it is assumed that a "crit. complex," generally a ring, is formed, which then dissociates into stable compounds. J. N. A.

Reaction mechanism of Marckwald's "asymmetric synthesis." F. EISENLOHR and G. MEIER (Ber., 1938, 71, [B], 997—1003).—Crystallisation of the brucine H salt of $\text{CMeEt}(\text{CO}_2\text{H})_2$ from MeOH has no effect on the asymmetric synthesis of $\text{CHMeEt}\cdot\text{CO}_2\text{H}$, so that the mixture of the two diastereoisomeric forms separates uniformly. The extent of the synthesis is not influenced by the rapidity of the decomp. of the salt. When the cryst. form of the salt is used the final acid is optically active whereas it is inactive if the amorphous or dissolved material is used. Decomp. of the non-cryst. strychnine, nicotine, or cinchonine salts in all cases gives an optically inactive final acid; similar results are observed when *d*- or *l*-methylbornylamine is used. It is concluded that Marckwald's "asymmetric synthesis" depends on the fact that the separation of the brucine H salt of $\text{CMeEt}(\text{CO}_2\text{H})_2$ and its homologues in cryst. form is accompanied by a displacement of the equilibrium of the two diastereoisomerides in accordance with their differing solubility. The rate of decomp. of the two forms is the same. According to the nature of the radicals at the asymmetric C the production of the *d*- or *l*-form as the more difficultly sol. is favoured and the excess of one form over the other is betrayed directly by the direction and magnitude of the rotation of the final acid. In solution, in the molten condition, and in the amorphous, glassy state the ratio 1:1 for both forms persists so that in accordance with the equal rates of decomp. of the diastereoisomerides the final products are optically inactive. H. W.

Asymmetric induction of E. Erlenmeyer. F. EISENLOHR and G. MEIER (Ber., 1938, 71, [B], 1004—1005; cf. A., 1912, i, 772).—If $\text{CMeEt}(\text{CO}_2\text{H})_2$ is heated with *d*-tartaric acid (I) at 170° and the product is treated with KOH-EtOH an optically inactive $\text{CHMeEt}\cdot\text{CO}_2\text{H}$ is obtained. The "induced activity" of Erlenmeyer is attributed to unhydrolysed esterific-

ation products which are optically active by reason of the participation of (I). The last experimental prop of the theory of asymmetric induction is thus withdrawn. H. W.

Resolution of racemates with the aid of molecular compounds. F. EISENLOHR and G. MEIER (Ber., 1938, 71, [B], 1005—1013).—Resolution through mol. compounds is not possible with the following pairs of substances partly because, contrary to the literature, the m.p. graph shows that mol. compounds are not formed and partly because division does not occur on crystallisation (in certain cases the more readily available optically active form is used in place of the racemic variety for determinations of m.p.): *d*-camphor (I) and *l*-menthol (II); *d*-OH-CHPh- CO_2H and (I); *d*-citronellal (III) and (II); (I) and (III); (I) and 3-hydroxy-4-methoxymandelic acid (IV); resorcylnmethylcarbinol (V) and (I); *d*-carvone and *d*-cinchonine (VI); (I) and (VI); *d*-amygdalin and (II). Anhyd. brucine (VII) and (V) give a mol. compound (1:2) which when cryst. from MeOH deposits mainly the compound of the *d*-carbinol, the isolation of which in optical homogeneity is somewhat difficult. The mother-liquors from these crops are conc. until on cooling there is no further tendency towards crystallisation; the residue after removal of solvent readily gives the pure *l*-carbinol. The possibility that the slightly acidic (V) forms a salt with the base is excluded since a similar product is not obtained with strychnine, (VI), or *l*-bornylmethylamine. The possibility of detecting the formation of mol. compounds by measurement of dielectric const. in dioxan is instanced by the examples, (I) and *o*-OH- $\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, (I) and *m*- $\text{C}_6\text{H}_4(\text{OH})_2$, (V) and (VII), (VII) and (II), (V) and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$. The prep. of (IV) from isovanillin and of (V) by electrolytic reduction of 2:4- $\text{C}_6\text{H}_3\text{Ac}(\text{OH})_2$ is described. H. W.

Stability of free radicals. C. E. H. BAWN (Trans. Faraday Soc., 1938, 34, 598—607).—The mechanism of decomp. of Et, Prⁿ, and Ac is discussed. Activation energies are computed for the reactions $\text{Et} \rightarrow \text{C}_2\text{H}_4 + \text{H}$, $\text{Pr}^n \rightarrow \text{C}_2\text{H}_4 + \text{Me}$, and $\text{Ac} \rightarrow \text{Me} + \text{CO}$. F. L. U.

Trimethylene diradical. C. E. H. BAWN and R. F. HUNTER (Trans. Faraday Soc., 1938, 34, 608—613).—The final products of the reaction of $\text{CH}_2(\text{CH}_2\text{Br})_2$ with excess of Na vapour are cyclopropane and $\text{CHMe}\cdot\text{CH}_2\cdot$ $[\text{CH}_2\text{I}_3]\cdot\text{Br}$ is formed as an intermediate stage, as shown by the isolation under suitable conditions of α -dibromo-*n*-hexane. No cyclohexane is produced. Normally the yield of cyclo-

propane + $\text{CHMe}\cdot\text{CH}_3$ is quant., and the latter is shown to be formed by a heterogeneous reaction at the walls of the vessel. The results are explicable only on the assumption that the $\cdot[\text{CH}_2]_3\cdot$ diradical is produced. The luminescence accompanying the reaction is discussed.

F. L. U.

Polymorphous forms of crystalline carbon compounds with long stretched chains, as determined by electron diffraction.—See A., 1938, I, 348.

Mercury-photosensitised decomposition of ethane.—See A., 1938, I, 366.

Thermal decomposition of hexane at high temperatures. J. N. PEARCE and J. W. NEWSOME (Ind. Eng. Chem., 1938, 30, 588—592).—When hexane was heated for a few min. or 1 hr. at 14,600 lb. per sq. in. the proportion of saturated hydrocarbons in the gaseous decomp. products was nearly const. up to 490° , these being mainly C_2H_6 (45–48%), CH_4 (24.5–26%), C_3H_8 (14.5–16.0%), and butanes (7.0–11.4%), whilst the small quantities of H_2 and of olefines decreased slowly with rising temp. Above 490°C deposition occurred and the amounts of CH_4 and C_2H_6 increased, and of all other products decreased, sharply. Similar behaviour was observed when the heating period was 2 hr., except that C deposition commenced at 460 – 470° . The fraction of the residual liquors (apart from undecomposed hexane) boiling below 100° was mainly aliphatic, whilst in that boiling above 200° the cycloparaffins predominated with appreciable quantities of aromatic and some olefinic compounds. The percentage of the two latter is the higher the higher is the temp. of decomp.

R. C. M.

Thermal decomposition of *n*-octane. R. F. MARSCHEMER (Ind. Eng. Chem., 1938, 30, 554—562).—The products of pyrolysis in Pyrex and stainless steel coils at atm. pressure and 570° consisted mainly of CH_4 (~25%), C_2H_4 (~27%), C_2H_6 (~17%), and C_3H_6 (~13%), with small quantities of various higher saturated and unsaturated hydrocarbons, but no H_2 or hexane. The composition was little affected by the extent of decomp. (between 18 and 33%), by the nature of the coil, or by conducting pyrolysis at 538° . Decomp. appears to be unimol., and the production of CH_4 without H_2 indicates that it occurs by way of free radicals, but the predictions of free radical theory as to the extent of olefine production do not agree well with the experimental results; the assumption of unequal splitting of the octyl radicals at the two possible points can explain the differences in the case of the higher members, but not the pronounced deficiency of C_2H_4 .

R. C. M.

Structural formulæ of unsaturated hydrocarbons.—See A., 1938, I, 346.

Synthesis of polyenes. R. KUHN (J.C.S., 1938, 605—614).—A lecture.

Fluorination of aliphatic substances by mercurous fluoride. A. L. HENNE and (Miss) M. L. RENOLL (J. Amer. Chem. Soc., 1938, 60, 1060—1061).—Pure HgF , prepared from HgO by way of HgNO_3 and Hg_2CO_3 and stored in Cu or resin, gives good

yields of alkyl fluorides from the iodides or bromides, but poor yields of polyfluorides from polyiodides. With CHMeBr_2 or $(\text{CH}_2\text{Br})_2$ it gives $\text{CH}_3\cdot\text{CHBr}$, with $\text{CH}_2\text{Br}\cdot\text{CHBr}_2$ gives a mixture of $\text{CH}_3\cdot\text{CBr}_2$ and $(\text{CHBr})_2$ with some $\text{CH}_2\text{Br}\cdot\text{CHBrF}$, and with $(\text{CHBr}_2)_2$ gives a very small yield of $\text{CHBr}_2\cdot\text{CHBrF}$. It reacts with polybromides only at 120 – 140° . It removes HCl from polychlorides. By addition of I it gives HgIF , which converts CHMeBr_2 into CHMeF_2 , CH_2I_2 into CH_2F_2 , $(\text{CH}_2\text{Br})_2$ into $\text{CHF}_2\cdot\text{CH}_2\text{Br}$ with some $\text{CH}_2\text{Br}\cdot\text{CHBrF}$, and $(\text{CHBr}_2)_2$ into $\text{CHBr}_2\cdot\text{CHF}_2$ with some $\text{CHBr}_2\cdot\text{CHBrF}$. With Cl_2 HgF gives HgClF , which is as effective as HgIF , but causes some side-reactions; e.g., it converts $(\text{CH}_2\text{Br})_2$ into $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{F}$ and $(\text{CH}_2\text{F})_2$ with some $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Br}$.

R. S. C.

Active atom in heptachloropropane. M. REBEK and G. MADRINO (Österr. Chem.-Ztg., 1938, 41, 49—52).—Reaction of $n\text{-C}_3\text{HCl}_7$ (I) with the base of crystal-violet, giving C_3Cl_6 and crystal-violet itself, is studied conductometrically (in COMe_2 ?). Reaction of (I) with $\text{C}_5\text{H}_5\text{N}$ is also studied. With MgMeI in Et_2O , (I) gives a pentachloropropylene, b.p. 70 – $71^\circ/12.5\text{ mm.}$, either $\text{CCl}_3\cdot\text{CH}\cdot\text{CCl}_2$ or $\text{CCl}_3\cdot\text{CCl}\cdot\text{CHCl}$. Zerevitinov determination with (I) shows 1 active H. Thus (I) behaves as a ψ -acid, comparable with MeNO_2 .

E. W. W.

Benzene derivatives. X. Addition of halogens and the additive products. So-called hexabromodihydrobenzene. T. VAN DER LINDEN (Rec. trav. chim., 1938, 57, 401—416).—“Hexabromodihydrobenzene” (I) prepared from xanthogallol (cf. Thomas and Moor, A., 1917, i, 460) with aq. or alcoholic NaOH or KOH , with NH_2Ph , $\text{C}_5\text{H}_5\text{N}$, or quinoline, and with Zn-EtOH , loses Br but yields no aromatic products. When heated with excess of Br, (I) yields three isomeric substances, $\text{C}_6\text{H}_2\text{Br}_8$, m.p. 94° , m.p. 153° (II), and m.p. 140 – 142° , and a substance, C_6HBr_9 , m.p. 165° . Heated to 300° , (II) yields C_6Br_8 (IV), whilst (I) at 230° gives (IV) and C_6HBr_5 . With excess of Cl_2 in sunlight, (I) yields dodecachlorohexane, m.p. 108 – 110° (also formed from $n\text{-C}_6\text{H}_{14}$ and Cl_2). It is suggested that (I) is $\alpha\beta\gamma\delta\epsilon\zeta$ -hexabromo- $\Delta^{4,5,6}$ -hexatriene, and (II) is $\alpha\alpha\beta\gamma\delta\epsilon\zeta$ -octabromo- $\Delta^{6,8}$ -hexadiene.

J. D. R.

Effect of deuterium substitution on colour. S. H. MARON and V. K. LAMER (J. Chem. Physics, 1938, 6, 299).—Addition of an equiv. quantity of Ba(OD)_2 to approx. 0.02N-protonitroethane in D_2O causes the reaction $2\text{EtNO}_2 + \text{Ba}^{++} + 2\text{OD}^- = 2\text{CHMe}\cdot\text{NO}_2 + \text{Ba}^{++} + 2\text{HOD}$. If an equiv. amount of D_2SO_4 is then added $2\text{CHMe}\cdot\text{NO}_2 + \text{Ba}^{++} + \text{D}_2\text{SO}_4 = 2\text{CHDMe}\cdot\text{NO}_2 + \text{BaSO}_4$. The solution remains colourless throughout, but on adding an equiv. quantity of Ba(OD)_2 the solution quickly becomes light yellow due to the reaction $2\text{CHDMe}\cdot\text{NO}_2 + \text{Ba}^{++} + 2\text{OD}^- = 2\text{CDMe}\cdot\text{NO}_2 + \text{Ba}^{++} + 2\text{HOD}$. The colour is discharged by D_2SO_4 and brought back by Ba(OD)_2 . The same operations on EtNO_2 in H_2O with Ba(OH)_2 and H_2SO_4 give colourless solutions throughout. EtNO_2 , $\text{CHDMe}\cdot\text{NO}_2$, $\text{CD}_2\text{Me}\cdot\text{NO}_2$, and $\text{CHMe}\cdot\text{NO}_2$ are shown to be colourless whilst $\text{CDMe}\cdot\text{NO}_2$ is pale yellow, absorbing from 5000—5200 Å. into the ultra-violet.

W. R. A.

Chemical reactions of organic compounds with X-ray-activated water.—See A., 1938, I, 366.

Identification of small amounts of isopropyl alcohol in alcohols. M. MÉTRA, L. LESAGE, and F. DESCATOIRE (Compt. rend., 1938, 206, 1026—1028).—The sample (50 c.c.) is treated with warm aq. Br followed by 30% NaOH (10 c.c.) and 12-vol. H_2O_2 (10 c.c.) and the whole is boiled for 5 min. The first 5 c.c. of distillate are tested for COMe_2 colorimetrically (Na nitroprusside- NH_3). A mixture of EtOH (99%) and Pr^iOH (1%) treated similarly gives tests for COMe_2 at all stages of the distillation. No EtOH obtained from natural sources gives a test for Pr^iOH .
J. L. D.

Structure of vinyl polymerides. II. Polyvinyl alcohol. C. S. MARVEL and C. E. DENOON, jun. (J. Amer. Chem. Soc., 1938, 60, 1045—1051; cf. A., 1938, II, 126).—Polyvinyl alcohol and HNO_3 give $\text{H}_2\text{C}_2\text{O}_4$, but no $(\text{CH}_2\text{CO}_2\text{H})_2$ (cf. A., 1927, 1051), and all its reactions indicate the α -glycol structure. It does not reduce HIO_4 at 0° ; $(\text{CHMe}\cdot\text{OH})_2$ and starch, but not $\text{CH}_2(\text{CHMe}\cdot\text{OH})_2$, reduce HIO_4 . With $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ it gives COMe_2 and AcOH . It and $\text{CH}_2(\text{CHMe}\cdot\text{OH})_2$, but not $(\text{CHMe}\cdot\text{OH})_2$, have an absorption max. at 2750 \AA . With H_3BO_3 it gives an indefinite, insol. complex (Na and Ca salts), formed by cross-linkings. An insol. oxalate is obtained, but only 8% of the OH is esterified and subsequent treatment with $\text{CH}_2\text{Cl}\cdot\text{COCl}$ left 25% free. It absorbs 4Br from H_2O , giving 3HBr and a product, $[\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})]_n$ or, less probably,

$[\cdot\text{CHBr}\cdot\text{C}(\text{OH})\langle\text{O}\rangle\text{CH}\cdot]_2$ which only slowly loses

HBr and with $p\text{-NO}_2\text{-C}_6\text{H}_4\text{CO}_2\text{Ag}$ in dioxan gives a product, $(\text{C}_{11}\text{H}_9\text{O}_6\text{N})_n$. Aq. Cl_2 gives similarly a product, $(\text{C}_4\text{H}_5\text{O}_2\text{Cl})_n$. The X-ray diagrams for stretched polyvinyl alcohol and its acetate indicate a regular structure.
R. S. C.

Rotatory power of allylpropenylcarbinol. D. DUVEEN and J. KENYON (Bull. Soc. chim., 1938, [v], 5, 704—709; cf. A., 1937, II, 146).— α -Allyl- Δ^2 -penten- β -ol (allylpropenylcarbinol), b.p. $64^\circ/18$ mm., with two isomeric radicals attached to the asymmetric C, gives a *dl*-H phthalate, m.p. $79\text{--}80^\circ$, converted, through the brucine salts [(+) form, m.p. 177° (decomp.), $[\alpha]_{\text{D}}^{25} -24^\circ$] by dil. HCl, into the (+)- (I) and (–)- (II) -H phthalates. (I) is decomposed, by blowing steam through an NaOH solution, into the (+)alcohol (III), b.p. $59^\circ/15$ mm. (acetate, b.p. $69^\circ/19$ mm.), which is reduced in Et_2O (Raney Ni) at 1.5 atm. to heptan- δ -ol ($\text{CHPr}^a\cdot\text{OH}$), b.p. $59^\circ/14$ mm. (II) is converted by HCO_2H (CHCl_3) and $\text{AcOH}\text{--NaOAc}$ into the (+)formate and (+)acetate, b.p. $65^\circ/12$ mm., respectively, with some racemisation. The parachor of (III) favours a ψ -cyclic rather than an open-chain configuration. Sp. vals. of $[\alpha]$ and their variation with temp. and nature of solvent are recorded.
A. T. P.

Dehydration of dialkylallylcarbinols. J. M. SLOBODIN (J. Gen. Chem. Russ., 1938, 8, 241—254).—The reactions: $\text{CRR}'\cdot\text{CR}''\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2 \leftarrow \text{CHRR}'\cdot\text{CR}''(\text{OH})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2 \rightarrow \text{CHRR}'\cdot\text{CR}''\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ ($\text{R} = \text{R}' = \text{H}$, $\text{R}'' = \text{Me}$;

$\text{R} = \text{H}$, $\text{R}' = \text{Me}$, $\text{R}'' = \text{Et}$; $\text{R} = \text{H}$, $\text{R}' = \text{Et}$, $\text{R}'' = \text{Pr}^a$; $\text{R} = \text{R}' = \text{Me}$, $\text{R}'' = \text{Pr}^a$) take place when the carbinol is warmed at 100° with dil. H_2SO_4 , or at $130\text{--}140^\circ$ with $\text{H}_2\text{C}_2\text{O}_4$, or by conversion into the chlorohydrin, followed by elimination of HCl by heating with $\text{KOH}\text{--EtOH}$; the chief product is in all cases that with a conjugated double linking system. These compounds with maleic anhydride give 3:3-dimethyl-, m.p. $132\text{--}134^\circ$, 3:3-diethyl-, m.p. $72\text{--}74^\circ$, and 3:3-diisopropyl-1:2:3:6-tetrahydrophthalic anhydride, m.p. 212° (decomp.). The structure of the products of dehydration of the carbinols was confirmed by identifying the products of ozonolysis.
R. T.

Linalool. I. Reaction with Japanese acid clay. T. MATUURA and B. MASUMOTO. II. Tetrahydrolinalool and sulphuric acid. T. MATUURA (J. Sci. Hiroshima Univ., 1938, 8, 121—128, 129—133).—I. Linalool, b.p. $86.5\text{--}87.5^\circ/12$ mm., passed at 15 g. per hr. over Japanese acid clay at $125\text{--}135^\circ/13\text{--}16$ mm., gives myrcene, (?) alloocimene (cf. Arbusov, A., 1934, 658), and dipentene; no geraniol or α -terpineol is detected. Hydrogenation of the hydrocarbons from the reaction (Pt-black-EtOH at room temp. and pressure or Ni in an autoclave) gives 68% of $\beta\zeta$ -dimethyloctane and 32% of *p*-menthane, indicating this ratio of chain to ring compounds.

II. Tetrahydrolinalool (I), b.p. $87.5\text{--}88^\circ/13$ mm., and 30% H_2SO_4 at 100° for 10 hr. give mainly $\beta\zeta$ -dimethyl- Δ^5 - and some Δ^6 -octene; (I) undergoes racemisation.
A. T. P.

Aliphatic alcohols of high mol. wt. T. ARENTZ and T. PEDERSEN (Tids. Kjemi, 1938, 18, 61—63).—Methods of prep. and uses are described.
M. H. M. A.

Stereochemistry of boric acid-diol derivatives.—See A., 1938, I, 298.

Aminobenzoic esters of glycol and of propane-diol. R. JACQUEMAIN and (MLLE.) G. DEVILLERS (Compt. rend., 1938, 206, 1305—1307).—Nitrobenzoates (cf. A., 1937, II, 148) in Et_2O with $\text{H}_2\text{--Pt-black}$ afford the corresponding aminobenzoates. The following are prepared: glycol di-o-, m.p. 126° (hydrochloride, m.p. 198° ; hydrobromide, m.p. 209° ; hydriodide, decomp. 188° ; picrate, m.p. 150°), di-m-, m.p. 146° (hydrochloride, m.p. 233° ; hydrobromide, m.p. 236° ; hydriodide, decomp. 167° ; picrate, m.p. 206°), and di-p-aminobenzoate, m.p. 206° ; propanediol di-o-, m.p. 89° (hydrochloride, m.p. 196° ; hydrobromide, decomp. 155° ; hydriodide, m.p. 171° ; picrate, m.p. 123°), di-m-, m.p. 94° (hydrochloride, m.p. 235° ; hydrobromide, m.p. $>230^\circ$; hydriodide, hygroscopic; picrate, m.p. 162°), and di-p-aminobenzoate, m.p. 137° (hydrochloride, m.p. $>230^\circ$; hydrobromide, m.p. $>230^\circ$; picrate, m.p. 164°).
J. L. D.

Synthesis of highly unsaturated glycols. (Interaction of esters of dibasic acids with allyl bromide and magnesium.) A. M. KURISCHKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1938, 4, 481—509).— $\text{Et}_2\text{C}_2\text{O}_4$, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$, and Mg in Et_2O yield $\delta\epsilon$ -diallyl- $\Delta^{\alpha\omega}$ -octadiene- $\delta\epsilon$ -diol, b.p. $117^\circ/8$ mm. $\delta\eta$ -Diallyl- $\Delta^{\alpha\omega}$ -decadiene- $\delta\eta$ -diol, b.p. $151\text{--}152^\circ/9.5$ mm., m.p. 27° , prepared similarly from $(\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$,

is oxidised (KMnO₄ in COMe₂ at -5°) to $\alpha\beta\delta\epsilon\kappa$ -hexahydroxy- $\Delta^{\alpha\kappa}$ -di-(β' - γ' -dihydroxypropyl)decane. 80-Diallyl- $\Delta^{\alpha\kappa}$ -undecadiene-80-diol, b.p. 150—152°/9 mm., m.p. 53.5—54.5°, and $\delta\mu$ -diallyl- $\Delta^{\alpha\kappa}$ -pentadecadiene- $\delta\mu$ -diol, b.p. 200—206°/7 mm., were prepared analogously from CH₂(CH₂·CO₂Et)₂ or [CH₂]₇(CO₂Et)₂. o-C₆H₄(CO₂Et)₂ gives similarly o-di-(α -hydroxy- α -allyl- Δ^{γ} -butenyl)benzene, decomp. 50—60°/8 mm. The above glycols yield unstable Br₈-derivatives.

R. T.

New octinene derivative. R. LESPIEAU (Bull. Soc. chim., 1938, [v], 5, 687—689).—In the prep. of $\delta\epsilon$ -dichloro- Δ^{α} -pentinen- γ -ol (A., 1928, 989) $\alpha\beta\eta\theta$ -tetrachloro- Δ^{δ} -octinene- $\gamma\zeta$ -diol, m.p. 139—139.5° (Ac₂ derivative, m.p. 93.5—94.5°) is also obtained; it is converted by 10% KOH into $\alpha\theta$ -dichloro- $\beta\gamma\zeta\eta$ -dioxido- Δ^{δ} -octinene (I), m.p. 59.8—60.3°, and a stereoisomeride, b.p. 193°/30 mm., 150—152°/2.5 mm., mixed with some (I). (I) refluxed with very dil. H₂SO₄ yields $\alpha\theta$ -dichloro- Δ^{δ} -octinene- $\beta\gamma\zeta\eta$ -tetraol, m.p. 130—131.5°, which with Ac₂O-KOAc at 155° for 10 hr. gives the Ac₆ derivative, m.p. 49—50°, hydrolysed by HCl in MeOH to Δ^{δ} -octinene- $\alpha\beta\gamma\zeta\eta\theta$ -hexaol, m.p. 145—146°.

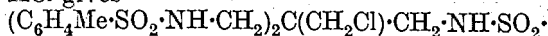
A. T. P.

Action of magnesium tert.-butyl chloride on ethyl sebacate, azelate, and suberate. A. D. PETROV and P. S. SANIN (J. Gen. Chem. Russ., 1938, 8, 195—198).—Et₂ sebacate, azelate, and suberate and MgBu^tCl in boiling xylene yield $\beta\beta\omega\omega$ -tetramethyl-tetradecane- $\gamma\mu$ -diol, m.p. 95—96°, $\beta\beta\mu\mu$ -tetramethyltridecane- $\gamma\lambda$ -diol, m.p. 78—80°, and $\beta\beta\lambda\lambda$ -tetramethyl-dodecane- $\gamma\kappa$ -diol, m.p. 108°, respectively.

R. T.

Raman spectrum and constitution of pentaerythritol.—See A., 1938, I, 296.

Amino-derivatives of pentaerythritol. F. G. MANN and A. LITHERLAND (Nature, 1938, 141, 789—790).—Tetrabromopentaerythritol heated with Na *p*-toluenesulphonamide (I) gives a good yield of the tetrasulphonamido-compound, C(CH₂·NH·SO₂·C₆H₄Me)₄ (II), m.p. 248°, which is readily hydrolysed (H₂SO₄) to C(CH₂·NH₂)₄. This can be isolated as C(CH₂·NH₂)₄·2H₂SO₄, which is almost insol. in H₂O. Contrary to the findings of Govaert (A., 1934, 638) the tetrahydrochloride of C(CH₂·NH₂)₄ can be recovered unchanged after (i) evaporation with H₂O for 36 hr., (ii) refluxing with HCl for 20 hr., and (iii) heating with HCl in a sealed tube for 5 hr. at 160°. Methylation of C(CH₂·NH₂)₄ readily yields C(CH₂·NMe)₄, which even with an excess of MeI gives only C(CH₂·NMe)₂(CH₂·NMe₃)₂. In the prep. of (II) a small amount of a trisulphonamide, C₂₆H₃₁N₃O₆S₃, m.p. 214°, is formed as a by-product; it gives C(CH₂·OH)(CH₂·NH₂)₃ on hydrolysis (H₂SO₄). HCl gives

C₆H₄Me

which, on complete hydrolysis followed by steam-distillation, yields (NH₂·CH₂)₂C<CH₂>NH. When heated with (I), C(CH₂Br)₃·CH₂·OAc gives a trisulphonamide, m.p. 171°, and the spirocyclic disulphonamide, C₆H₄Me·SO₂·N<CH₂>C<CH₂>N·SO₂·C₆H₄Me, m.p. 185°. On hydrolysis (HCl) followed by steam-dis-

tillation both these compounds yield the spirocyclic diamine NH<CH₂>C<CH₂>NH.

L. S. T.

Synthesis of diisopropyl ether. I—IV. M. KATUNO (J. Soc. Chem. Ind. Japan, 1938, 41, 75B—82B).—The yields of C₃H₈ and Pr₂O from PrⁿOH and H₂SO₄ have been measured under varying conditions. PrⁿO is best obtained (48%) with 96% H₂SO₄ at 97—98°. High yields of C₃H₈ (up to 81.5%) are obtained with stirring or in presence of porous solids. The reaction mechanism is discussed.

A. L.

Synthesis of β -chloro-ethers by the chloroamide method. M. V. LICHOSCHERSTOV and T. V. SCHALAEVA (J. Gen. Chem. Russ., 1938, 8, 370—380).—The ethers CHMeCl·CHMe·OR (R = Me, b.p. 118—118.4°, Et, b.p. 131—133°, Buⁿ, b.p. 165—166°, and isoamyl, b.p. 187—188.6°), and CH₂Cl·CHEt·OR (R = Me, b.p. 120.5—121°, Et, b.p. 140—142°, Prⁿ, b.p. 154—156°, Buⁿ, b.p. 177—179°, Bu^s, b.p. 169—170°, and isoamyl, b.p. 191.5—194°) are described.

R. T.

Conjugated systems. VI. Reaction of divinyl with alkyl hypobromites, and synthesis of alkoxyprenes. A. A. PETROV (J. Gen. Chem. Russ., 1938, 8, 208—215).—Divinyl in ROH and PhSO₂·NBr₂ yield the ethers CH₂:CH·CH(OR)·CH₂Br [R = H, b.p. 160—160.5°; Me, b.p. 142.5—143° Et (I), b.p. 153.5—154.2°; Prⁿ (II), b.p. 58—58.5°/10 mm., Buⁿ, b.p. 73.5—74°/10 mm.; Bu^s, b.p. 63—63.5°/10 mm., isoamyl, b.p. 81—81.5°/10 mm.], from which HBr is eliminated by boiling with KOH in EtOH, to yield the corresponding alkoxyprenes, CH₂:CH·C(OR):CH₂, of which β -isoamylloxy- Δ^{γ} -butadiene, b.p. 69.5—70°/54 mm., is new. (I) in CHCl₃ and Cl₂ yield $\gamma\delta$ -dichloro- α -bromo- β -ethoxybutane, b.p. 104—104.5°/10 mm. With Br, (I) or (II) gives $\alpha\gamma\delta$ -tribromo- β -ethoxy-, b.p. 127°/10 mm., or -propoxy-butane, b.p. 137°/10 mm.

R. T.

Di- and tri-ethers [of ethylene and diethylene glycols]. L. LISTON and W. M. DEHN (J. Amer. Chem. Soc., 1938, 60, 1264).—Ethers, OH·[CH₂]₂·OR and OH·[CH₂]₂·O·[CH₂]₂·OR, give diethers when heated with "powdered" Na and the alkyl halide. The diethers are not stable, particularly the diallyl ethers, which may explode when distilled. Ethylene glycol Et allyl, b.p. 139—142°, Et n-amyl, b.p. 180—183°, Bu allyl, b.p. 183—184°, Bu n-amyl, b.p. 221—222°, and Et·Bu ether, b.p. 164—165°, and diethylene glycol Et allyl, b.p. 200—203°, Et Bu, b.p. 218—219°, and Et n-amyl ether, b.p. 121—124°/18 mm., are prepared.

R. S. C.

Desaturation products from $\alpha\gamma\gamma$ -trimethoxybutane. R. O. NORRIS, J. J. VERBANC, and G. F. HENNING (J. Amer. Chem. Soc., 1938, 60, 1159—1161).—OMe·[CH₂]₂·CMe(OMe)₂ (I) is obtained in the yield stated from (a) OMe·[CH₂]₂·C·CH 56, CH₂:CH·C·CH 65, or OMe·CH₂·C·CMe 57% by heating with a little HgO and BF₃ in MeOH, or (b) from CH₂:CH·CMe(OMe)₂ (II) 88, $\alpha\gamma$ -dimethoxy- Δ^{δ} -butene (III), b.p. 130°/748 mm., 96, or β -methoxybutadiene (IV), b.p. 75°/748 mm., 92% in MeOH at room temp. in presence of a trace of *p*-C₆H₄Me·SO₃H. With a

trace of NaHSO_4 at 150° (I) gives 60% of (IV) and 29% of (II), (IV) being obtained under similar conditions in 85% yield from (II). With a little H_3BO_3 at 140 – 150° (I) gives 66% of (III); at 300 – 320° alone it yields (III). Oxidation of (IV) by KMnO_4 gives only a little $\text{CH}_2\text{Ac}\cdot\text{CH}_2\cdot\text{OMe}$, $\text{CH}_2\cdot\text{CH}\cdot\text{COMe}$, and AcOH , and its structure is doubtful.

R. S. C.

Electrochemical "nitration." [Ester formation from ethylene.]—See A., 1938, I, 365.

Anomalous elimination of sulphur dioxide. P. NYLÉN (Tids. Kemi, 1938, 18, 59–61).— EtSO_3Cl (I) and $(\text{OEt})_2\text{P}\cdot\text{ONa}$ (II) in EtOH give $(\text{OEt})_2\text{PO}$ (III) and SO_2 . (I) and (II) in Et_2O or C_6H_6 give mainly $(\text{OEt})_4\text{P}_2\text{O}_3$ and SO_2 (42% of the S present), but also $(\text{OEt})_2\text{SO}$, $(\text{OEt})_4\text{P}_2\text{O}_2$, and (III). M. H. M. A.

Characterisation of carboxylic acids as ureides by aid of carbodi-imide. F. ZETTSCHKE, E. LÜSCHER, and H. E. MEYER (Ber., 1938, 71, [B], 1088–1093).—Carboxylic acids are converted into the corresponding monoureides by heating with a carbodi-imide, preferably carbodi-*p*-tolylimide, in Et_2O , benzenoid hydrocarbons, light petroleum, CHCl_3 , CCl_4 , COMe_2 , or $\text{C}_5\text{H}_5\text{N}$. Possible complications arise from the decomp. of the monoacylated carbamide into acid anhydride and carbimide, the direct production of acid anhydride and diarylcarbamide, and the polymerisation of the imide. The first reaction can be used for further identification of the ureide by converting it into the arylide, generally by boiling *sec*-octyl alcohol. The following are described: the *Bz*, m.p. 128 – 129° , and *stearyl*, m.p. 79° , derivatives of $\text{CO}(\text{NHPh})_2$; the *trichloroacetyl*, m.p. 118 – 122° (decomp.), *tetrol*, m.p. 124° , *heptol*, m.p. 125° , *nonol*, m.p. 97° , *palmityl*, m.p. 94 – 95° , *stearyl*, m.p. 94° , α -*bromostearyl*, m.p. 87° , *brassidyl*, m.p. 81° , *erucyl*, m.p. 50° , *Bz*, m.p. 159° , *phenylpropionyl*, m.p. 200 – 204° , *hippuryl*, m.p. 151° , *m-nitrobenzoyl*, m.p. 197° , *p-dimethylaminobenzoyl*, m.p. 142 – 144° , *cinnamyl*, m.p. 125° , *p-acetoxybenzoyl*, m.p. 115 – 120° , α -*phenylcinchonyl*, m.p. 191 – 194° , $2':4'$ -*dimethoxybenzophenone-2-carboxyl*, m.p. 143 – 145° , *diacetylresorcylyl*, m.p. 126 – 128° , *suberyl*, m.p. 182° , *sebacyl*, m.p. 170 – 171° , *phellogenyl*, m.p. 169° , *eicosanedicarboxyl*, m.p. 172° , *fumaryl*, m.p. 171 – 172° , *phellonyl*, m.p. 139 – 140° , *phloionolyl*, m.p. 155 – 156° , *phloionyl*, 179 – 180° , derivatives of $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}\cdot p)_2$; the *stearyl*, m.p. 94° , α -*crotonyl*, m.p. 128° , ω -*undecenyl*, m.p. 84 – 85° , *oleyl*, m.p. 42 – 43° , *Bz*, m.p. 197° , derivatives of $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}\cdot p)_2$; the *stearyl*, m.p. 134° , *oleyl*, m.p. 93° , and *Bz*, m.p. 215° , derivatives of $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{I}\cdot p)_2$; the *stearyl*, m.p. 94° , and *Bz*, m.p. 165° , compounds of *s*-di-2-naphthylcarbamide; *di-p-bromophenylcarbamide*, m.p. 275 – 277° . H. W.

[Preparation of] esters by automatic processes without catalysts. T. R. LISTON and W. M. DEHN (J. Amer. Chem. Soc., 1938, 60, 1264–1265).—The Betz–Holden apparatus for the automatic prep. of esters is modified and then gives excellent yields. *n*-, b.p. $196^\circ/756$ mm., $105^\circ/35$ mm., *sec*-, b.p. $185^\circ/756$ mm., $93^\circ/27$ mm., and *tert*-*amyl*, b.p. $168^\circ/756$ mm., $88^\circ/43$ mm., and *CMeEt*₂ *chloroacetate*, b.p. $184^\circ/756$ mm., $93^\circ/30$ mm., *n*-, b.p. $207^\circ/756$ mm., $124^\circ/48$ mm., *sec*-, b.p. $198^\circ/756$ mm., $93^\circ/20$ mm., and *tert*-

amyl, b.p. $180^\circ/756$ mm., $93^\circ/30$ mm., and *CMeEt*₂ *dichloroacetate*, b.p. $197^\circ/756$ mm., $105^\circ/40$ mm., *n*-, b.p. $218^\circ/756$ mm., $118^\circ/30$ mm., *sec*-, b.p. $206^\circ/756$ mm., $108^\circ/30$ mm., and *tert*-*amyl*, b.p. $191^\circ/756$ mm., $105^\circ/30$ mm., and *CMeEt*₂ *trichloroacetate*, b.p. $201^\circ/756$ mm., $105^\circ/25$ mm., are described. R. S. C.

Preparation of esters. V. M. MITCHOVITCH (Bull. Soc. Chim. Yougoslav., 1937, 8, 157–168).—Et esters of aliphatic and aromatic carboxylic acids are obtained in good yield by adding PhMe and 1–2% of H_2SO_4 to the acid–EtOH mixtures, and heating gently, when the H_2O formed is distilled off as a H_2O –EtOH–PhMe azeotrope. R. T.

Secondary reactions in the condensation of organomagnesium compounds with aliphatic esters. M. TUOT (Compt. rend., 1938, 206, 1124–1126).—*sec*. Alcohols do not always arise from secondary reactions of esters with Mg org. compounds. If the initial reaction is substitution of OEt with formation of a Me ketone, the secondary products are the Mg enolate of this ketone together with the corresponding ketol and a saturated hydrocarbon. If the initial product is a ketone with poly-carbon radicals, the secondary products are the corresponding *sec*. alcohol together with an ethylenic hydrocarbon. It is concluded that a secondary reaction occurs when there is a *tert*. C atom either in the Mg derivative in the *ortho*-, α -, or β -position, or in the ketone in the α - or β -position, and that the direction of this reaction depends solely on the nature of this ketone. The amount of secondary product diminishes as the *tert*. C atom is removed. The simultaneous presence of *tert*. C atoms in the α -position in both reactants leads to a small yield of *tert*. alcohol, and of *tert*. C atoms in the *ortho*-position in the Mg derivative and in the α -position in the ketone, to production of the secondary products only. E. G. B.

Influence of contact poisons on the direction of heterogeneous catalytic reactions.—See A., 1938, I, 364.

Preparation of α -chlorocrotonic acid. J. C. ROBERTS (J.C.S., 1938, 779; cf. Krämer and Pinner, A., 1871, 556).—Butylchloral hydrate is shaken with HNO_3 and the solution distilled, the residue $(\text{CCl}_3[\text{CH}_2]_2\cdot\text{CO}_2\text{H})$ yielding 83.5% of $\text{CHMe}\cdot\text{CCl}\cdot\text{CO}_2\text{H}$, new m.p. 99 – 100° [Et ester, new b.p. 174 – 176° (corr.)], when heated with Zn dust. E. G. B.

α -Bromo-*n*-butyric acid. III. Is there more than one racemic α -bromo-*n*-butyric acid? R. AHLBERG (J. pr. Chem., 1938, [ii], 151, 35–44; cf. A., 1933, 257).—The heterogeneity of *dl*- $\text{CHEtBr}\cdot\text{CO}_2\text{H}$ is supported by slow and incomplete crystallisation of its cinchonidine salt and by transformation of its morphine salt into a less sol. variety. The α -*p*-tolyl-, α -*p*-bromophenyl-, and α -1-naphthyl-ethylamine salts are dimorphic. R. S. C.

Preparation of isomeric *cis*-pentenoic acids. E. SCHJÄNBERG (Svensk Kem. Tidskr., 1938, 50, 98–101).—Hydrogenation of Δ^a - and Δ^b -pentenoic acids at room temp. (PdCl_2 and gum arabic) gave respectively 80% yields of *cis*- Δ^a -pentenoic acid, m.p. $< -20^\circ$, b.p. $94^\circ/23$ mm., and *cis*- Δ^b -pentenoic acid,

m.p. $< -20^\circ$, b.p. $80.5^\circ/15$ mm. No *trans*-acids could be isolated. M. H. M. A.

Heats of combustion, refractive data, and alkaline hydrolysis of the ethyl *cis*-pentenoates. E. SCHJÄNBERG (Svensk Kem. Tidskr., 1938, 50, 102—106; cf. preceding abstract).—The alkaline hydrolysis has been studied, and the heats of combustion, d_4^{20} , n_D^{20} , and $[R]_D^{20}$ determined, of *Et cis*- Δ^1 -pentenoate, b.p. 147° , and *Et cis*- Δ^2 -pentenoate, b.p. 138.5° . The vals. are discussed in comparison with those for the corresponding *trans*-compounds (A., 1937, I, 309, 416). M. H. M. A.

Electrolysis of salts of heptioic acid alone or mixed with nitrates. F. FICHTER and O. LEUPIN (Helv. Chim. Acta, 1938, 21, 616—625).—Electrolysis of $n\text{-C}_6\text{H}_{13}\cdot\text{CO}_2\text{K}$ gives mainly $\text{C}_{12}\text{H}_{26}$ with smaller amounts of Δ^1 -hexene, $n\text{-C}_5\text{H}_{11}\cdot\text{CHO}$, COMeBu^a , $\text{C}_5\text{H}_{11}\cdot\text{CO}_2\text{H}$, $n\text{-C}_6\text{H}_{13}\cdot\text{OH}$, $\text{CHMeBu}^a\cdot\text{OH}$, $n\text{-C}_6\text{H}_{13}\cdot\text{CO}_2\text{C}_6\text{H}_{13}$, and a dodecyl heptate, yielding a dodecanol (I), b.p. $118\text{—}120^\circ/13$ mm. In presence of NaNO_3 it gives also mainly $\text{C}_{12}\text{H}_{26}$ with a little C_6H_{12} and esters yielding $n\text{-C}_6\text{H}_{13}\cdot\text{OH}$ and (I). Formation of esters of (I) is due to addition of C_6H_{12} to esters of $n\text{-C}_6\text{H}_{13}\cdot\text{OH}$. Diheptoyl peroxide (prep. from the anhydride and Ba_2O_2), decomp. about 88° , yields, when exploded at 250° , 95% of CO_2 and 94% of $\text{C}_{12}\text{H}_{26}$, and, when slowly decomposed, much CO_2 with $\text{CHMeBu}^a\cdot\text{OH}$, $n\text{-C}_6\text{H}_{13}\cdot\text{OH}$, COMeBu^a , and $\text{C}_6\text{H}_{13}\cdot\text{CO}_2\text{C}_6\text{H}_{13}$, but no (I). R. S. C.

"Peroxide" or "oxygen" effect. II. J. C. SMITH (Chem. and Ind., 1938, 461—466; cf. A., 1937, II, 438).—Mainly a review of recent work. The following is new. The speed of "normal" addition of HBr to Δ^1 -undecenoic acid in C_6H_6 or hexane can be reduced to 0.02 of that of the "abnormal" reaction. In 0.02M solution in C_6H_6 the "abnormal" reaction is induced by Br (liquid or liberated from HBr by peroxides), but this is probably due to traces of O_2 , as Br alone is ineffective in 0.45M solution. $\text{CMe}_2\cdot\text{CH}\cdot\text{C}$ yields only $\text{CMe}_2\cdot\text{Br}\cdot\text{CH}_2\cdot\text{C}$. It is concluded that O_2 is essential for the abnormal reaction, but that BzO_2H , Br , etc. act as subsidiary catalysts. R. S. C.

Specific volumes of dilute sodium oleate solutions.—See A., 1938, I, 356.

Metal soaps and gelation of their paraffin solutions.—See A., 1938, I, 356.

Transformation of cyclic esters into linear polyesters. S. BEZZI (Gazzetta, 1398, 68, 215—224).—The degree of polymerisation of the H_2O -insol. polylactylic acids (I) formed by heating anhyd. lactide (II) at 200° is followed by titrating (I) with NaOEt in COMe_2 at -10° (phenolphthalein). It is a max. after 135 hr., after which there is depolymerisation; this is taken as evidence of a hydrolysis-esterification mechanism, and not that proposed by Carothers. The yield of polymerides and the proportion of free CO_2H groups are tabulated, both with anhyd. (II) and in presence of H_2O . E. W. W.

Production of maleic acid by catalytic oxidation of benzene. G. I. KIPRIANOV and F. T. SCHOSTAK (J. Appl. Chem. Russ., 1938, 11, 471—

480).— C_6H_6 -air mixture is passed over a no. of catalysts at $350\text{—}500^\circ$; the most active catalyst was $7:3:0.5 \text{ V}_2\text{O}_5\text{—MoO}_3\text{—Co}_2\text{O}_3$, at 450° . Replacement of Co_2O_3 by NiO , Cr_2O_3 , Fe_2O_3 , or MnO lowered the yield of maleic acid, as did also omission of MoO_3 . The max. yields obtained with 50:1 air- C_6H_6 mixture, and passing the residual gas through a second layer of catalyst, were 80—85%. R. T.

Oxalic ester method for the synthesis of polyenedicarboxylic acids. R. KUHN and J. MICHEL (Ber., 1938, 71, [B], 1119—1126; cf. A., 1936, 1093).— Et tiglate, $\text{Et}_2\text{C}_2\text{O}_4$, and KOEt in anhyd. Et_2O give the *K* derivative (I) of *Et* ethoxalyl-tiglate, transformed by Ac_2O in boiling Et_2O into *Et* $_2$ α -acetoxy- α' -methylmuconate, b.p. $175^\circ/12$ mm.; this is converted by Al-Hg and H_2O in Et_2O into a mixture of *Et* $_2$ α -acetoxy- α' -methyl- and *Et* $_2$ α -methyl-dihydro-muconate from which α -methylmuconic acid, m.p. 279° , and α -methyl-dihydromuconic acid, m.p. 158° , were isolated. The replacement of Ac by H during hydrogenation by Al-Hg appears general and is preceded by the formation of the acetyldihydro-ester, which is unstable towards excess of amalgam. The structure of the mol. must be such that the formation of AcOH is possible. Thus 9-acetoxyfluorene is resistant towards Al-Hg whereas dihydroanthraquinol diacetate readily yields anthracene. (I) and the similar compound from *Et* angelate yield the same *p*-nitrobenzoate [*Et* $_2$ α -*p*-nitrobenzoyl- α' -methylmuconate], m.p. 101° . Probably, therefore, the condensation with $\text{Et}_2\text{C}_2\text{O}_4$ is accompanied by a displacement of the double linking but this is not completely proved. Attempts to obtain β -phenylmuconic acid from *Et* β -phenylcrotonate were fruitless. The *K* derivative from $\text{Et}_2\text{C}_2\text{O}_4$ and $\text{CMe}_2\cdot\text{CMe}\cdot\text{CO}_2\text{Et}$ could not be acetylated whilst *Et* Δ^1 -nonenoate, b.p. $118\text{—}120^\circ/12$ mm. (obtained by the action of P_4O_{10} on *Et* β -hydroxynonoate, b.p. $138\text{—}140^\circ/12$ mm., derived from *n*-heptaldehyde, $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Et}$, and Zn turnings in C_6H_6), does not appear to give a *K* derivative even after addition of $\text{C}_5\text{H}_5\text{N}$. *Et* α -phenylcrotonate yields the *K* derivative of *Et* ethoxalyl- α -phenylcrotonate, whence *Et* $_2$ α -acetoxy- α' -phenylmuconate, m.p. 62° . This gives α -phenylmuconic acid (II), m.p. 265° , hydrogenated to α -phenyladipic acid, and, as by-product, α -phenyldihydromuconic acid, m.p. 171° , also obtained by the action of Na-Hg on (II) and ozonised to BzOH and $(\text{-CH}_2\cdot\text{CO}_2\text{H})_2$ so that addition occurs in the $\alpha\beta$ and not in the $\alpha\delta$ positions. Crotonaldehyde cannot be satisfactorily condensed with $\text{Et}_2\text{C}_2\text{O}_4$ as it reacts too readily in other directions, but tiglaldehyde gives a *K* derivative (III), converted by cautious treatment with dil. HCl and Et_2O into ethoxalyl-tiglaldehyde, m.p. 95° (semicarbazone, m.p. 203°), which immediately reduces cold $\text{Ag}_2\text{O-NH}_3$ and reddens fuchsin- H_2SO_3 . With Ac_2O in Et_2O (III) yields ethoxalylacetyltiglaldehyde (semicarbazone, m.p. 217°). $\text{CH}_2\text{Ph}\cdot\text{CHO}$, MeCHO , and NaOAc in $\text{H}_2\text{O-EtOH}$ at 110° give α -phenylcrotonaldehyde, b.p. $233\text{—}235^\circ/750$ mm., in 50% yield; this with $\text{Et}_2\text{C}_2\text{O}_4$ and KOEt gives a *K* derivative, from which "*ethoxalyl- α -phenylcrotonaldehyde*," $\text{C}_{14}\text{H}_{14}\text{O}_4$, m.p. 164° , is derived. The constitution of the compound is uncertain since it does not reduce $\text{NH}_3\text{-Ag}_2\text{O}$, does not

red den fuchsin- H_2SO_3 , and does not appear to yield a semicarbazone. H. W.

Condensation of dicarboxylic esters with ethyl oxalate in presence of sodium. I. Condensation of azelaic with oxalic ester. M. A. ZAKUTSKAJA and R. A. GUDOVITSCH. **II. Condensation of suberic with oxalic ester.** M. A. ZAKUTSKAJA and V. G. GLOBIN (J. Gen. Chem. Russ., 1938, 8, 216—221, 222—224).—I. Et_2 azelate in EtOH , Na, and $\text{Et}_2\text{C}_2\text{O}_4$ (10 hr. at room temp., 16 hr. at 40°) yield Et_2 α -ethoxalylazelate (not isolated), converted by distillation into Et_3 heptane- $\alpha\alpha\eta$ -tricarboxylate, b.p. 180 — $185^\circ/8$ mm., which with boiling 20% KOH gives azelaic acid, with EtI in EtOH in presence of Na yields Et_3 nonane- $\gamma\gamma$ -tricarboxylate, b.p. 185 — $186^\circ/10$ mm., and with NH_3 in EtOH (20 hr. at 115 — 120°) gives heptane- $\alpha\alpha\eta$ -tricarboxylamide, m.p. 140 — 142° .

II. Et_2 suberate and $\text{Et}_2\text{C}_2\text{O}_4$ give similarly Et_3 hexane- $\alpha\alpha\zeta$ -tricarboxylate, b.p. 182 — $187^\circ/15$ mm., converted into suberic acid by boiling 20% KOH.

R. T.

cis-Aconitic acid. G. SEMERANO and L. SARTORI (Gazzetta, 1938, 68, 167—173).—*cis*-Aconitic acid (A., 1929, 172) has the dissociation const. 1.13×10^{-2} ; at the Hg - H_2O interface the depolymerisation const. 1.7×10^{-3} suggests 0.88 depolymerisation to the labile mol. $\text{CH}\cdot\text{CO}_2\text{H}$ (cf. A., 1938, I, 250; II, 169). E. W. W.

d-Ascorbic acid from d-sorbose. K. GÄTZI and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 456—463).—*d*-Sorbose (I), m.p. about 154° , prepared from *d*-galactose, contained so much *d*-tagatose that, after conversion into the diisopropylidene compound and oxidation, only a little diisopropylidene-*d*-tagat-uronic acid was isolated. (I), m.p. 160 — 165° (prepared from *d*-gulose), gives diisopropylidene-*d*-gulosonic acid, cryst., and thence *d*-gulosonic (α -keto-*d*-gulonic) acid, m.p. 173 — 174° (decomp.; corr.) [*Me* ester, m.p. 147 — 155° (corr.)], and *d*-ascorbic acid. The synthesis is not, however, economic. R. S. C.

Colorimetric determination of ascorbic acid.—See A., 1938, III, 598.

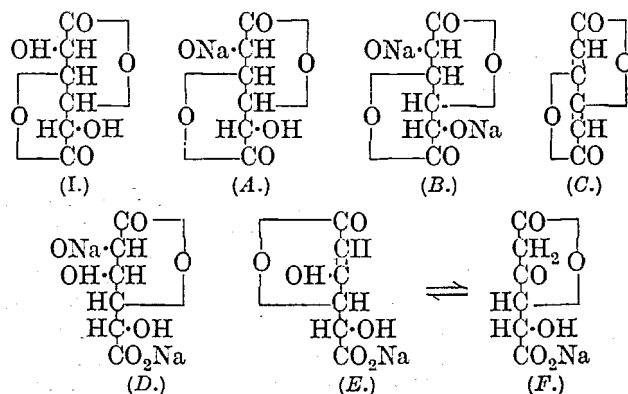
Spectra of l-ascorbic, hydroxytetrone, reductic, and α -crotonic acid.—See A., 1938, I, 342.

Synthesis of hexane- $\alpha\beta\epsilon\zeta$ -tetracarboxylic acid. P. C. GUHA and C. KRISHNAMURTHY (Current Sci., 1938, 6, 503—504; cf. A., 1936, 1252).— $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ and $(\text{CH}_2\text{Br})_2$ or $[\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2]_2$ and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ yield Et_6 hexane- $\alpha\beta\epsilon\zeta$ -hexacarboxylate, which when boiled with dil. HCl yields hexane- $\alpha\beta\epsilon\zeta$ -tetracarboxylic acid, m.p. 177 — 178° (Et_4 ester, b.p. 195 — $205^\circ/2$ mm.).

A. Li.

Reaction of d-mannosaccharodilactone with alkali. K. REHORST (Ber., 1938, 71, [B], 923—932; cf. A., 1937, II, 86).—Under the most favourable conditions *d*-mannosaccharodilactone (I) (1 mol.) reacts with I (4 atoms) giving CHI_3 and $\text{H}_2\text{C}_2\text{O}_4$ in amount corresponding with 19.50% and 10.73% of (I) whilst Na_2 *d*-mannosaccharate (II) is obtained in 50% yield. Reaction appears to occur only with NaOH and I; pre-formed NaOI does not give CHI_3 or

$\text{H}_2\text{C}_2\text{O}_4$ so that a preliminary addition of I at a double linking is assumed. It is considered that (I) passes



primarily into A, which by opening of the lactone rings is converted partly into (II). A second portion of A passes through B into C, which is completely degraded to H_2O and CO_2 . A third portion passes through D into E, which gives $\text{H}_2\text{C}_2\text{O}_4$ and mesotartaric (III) or erythronic acid (IV). E is in equilibrium with F, which becomes converted into CO_2 , CHI_3 , and (III). (III) has not been analytically detected but the formation of (IV) is rendered probable by the isolation of the corresponding γ -lactone. The unusual behaviour of (I) depends on the acidic character of OH at $\text{C}_{(2)}$ and $\text{C}_{(5)}$, which is ascribed to the overlapping O bridges. The reduction of Fehling's solution and the consumption of I by *d*-mannuronolactone is partly due to the CHO group, partly to the overlapping bridges. The inability of glucurone to give CHI_3 with I and KOH and the absence of mutarotation are ascribed to the presence of a free CHO; in support of this view it adds dimethylhydroresorcinol to give a compound, $\text{C}_{22}\text{H}_{30}\text{O}_9\cdot\text{H}_2\text{O}$, m.p. 140 — 141° after softening at 135° , whereas *d*-glucuronic acid does not react with dimedon and hence exists in the semiacetal form. In accordance with expectations, CHI_3 is produced less copiously from the $\gamma\delta$ -dilactone, *d*-saccharodilactone, than from the $\gamma\gamma$ -dilactone (I). H. W.

Polarimetric examination of the thiol-disulphide system. T. BERSIN and J. STEUDEL (Ber., 1938, 71, [B], 1015—1024).—It is shown polarimetrically that the change $2\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I) + $[\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}]_2$ (II) = $(\text{S}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ (III) + $2\text{SH}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ (IV) is an equilibrium reaction which follows the law of mass action. The const. is approx. 1 and the diminution of free energy is therefore nearly 0. From the viewpoint of energy the systems (I)/(III) and (II)/(IV) are almost equiv. On either side the rate increases uniformly with p_{H} and temp. The unimol. course and the difference between the velocity coeff. of the forward and reverse reaction suggest that the change is governed by the degree of dissociation of the SH-compound into RS^- and H^+ . H. W.

Photolysis of aliphatic aldehydes. VI. Acetaldehyde.—See A., 1938, I, 366.

Reactions of aldehydes with alcohols. B. N. RUTOVSKI and K. S. ZABRODINA (J. Appl. Chem. Russ., 1938, 11, 302—310).—Aldehydes $\text{CH}_2\text{R}\cdot\text{CHO}$,

but not $\text{ClRR}'\cdot\text{CHO}$, react at room temp., and in presence or absence of solvent, with alcohols, $\text{CH}_2\text{R}\cdot\text{OH}$ or $\text{CHRR}'\cdot\text{OH}$ but not $\text{CRR}'\text{R}''\cdot\text{OH}$, to give semi-acetals, which are less sol. in 70% EtOH than are either of their components; the n and d of the products thus separated are identical with those of 1:1 alcohol-aldehyde mixtures, whence it is concluded that the reaction proceeds to completion in such conditions.

R. T.

Structure of some halogenated aldehydes and of a methoxy-derivative. A. KIRRMANN and J. LICHTENBERGER (Compt. rend., 1938, 206, 1259—1261).—Certain α -bromoaldehydes (cf. A., 1929, 795) which give no phenylhydrazones and $\alpha\beta$ -dichloro- α -ethylhexaldehyde (I) give Raman spectra which show evidence of the :CO linking. (I) with NaOMe affords $\alpha\beta$ -oxido- $\alpha\gamma$ -dimethoxy- β -ethylhexane, the Raman spectrum of which shows no evidence of a :CO linking but a line characteristic of an ethylene oxide type of structure.

J. L. D.

Polymerisation of methylglyoxal. L. DE V. MOULDS and H. L. RILEY (J.C.S., 1938, 621—626; cf. A., 1932, 1875).—Mol. wt. determinations of pure, freshly-distilled AcCHO (I) (cf. A., 1926, 599; 1932, 833) in solution indicate that it is monomeric in H_2O and C_6H_6 . Physical data are recorded. The n indicates presence of both keto- and enolic forms. Values of n for aq. solutions show a sharp max. at 93.5% of (I), not indicating any definite hydrate. The parachor indicates a mixture of the mono- and the di-meride. (I) explodes spontaneously under pressure in O_2 , probably owing to peroxide formation, but not when polymerised. Heats of combustion of (I) and of its polymerised forms show that polymerisation occurs with evolution of 8 kg.-cal. per mol. in 11 weeks. Polymerisation is greatly accelerated by traces of H_2O . It probably consists of interaction of (I) with H_2O to yield CHAc(OH)_2 , which then polymerises to $(\text{OH}\cdot\text{CHAc})_2\text{O}$, etc.

E. G. B.

Derivatives of the oxidation products of glycerol. II. H. P. DEN OTTER (Rec. trav. chim., 1938, 57, 427—436).— AcCHO can be prepared from $\text{CO}(\text{CH}_2\text{OH})_2$ with $\text{H}_2\text{SO}_4\text{--Al}_2(\text{SO}_4)_3$, but cannot be regenerated from its ω -phenylhydrazone by boiling with PhCHO , Ac_2 , or alone in xylene. The following are described: methylglyoxal- ω - α -naphthylhydrazone, m.p. 161°, and -4:6-dinitro-3-ethoxyphenylhydrazone, m.p. 161—163°, -o-nitro-, m.p. 233°, -m-nitro-, m.p. 261°, -5-chloro-2-nitro-, m.p. 280—282°, -5-bromo-2-nitro-, m.p. 300—301° (decomp.), -4:6-dinitro-3-ethoxy-, m.p. 294°, -4-bromo-, m.p. 178°, -diphenyl-, m.p. 180°, -phenylbenzyl-osazone, m.p. 129°, -o-, m.p. 122°, -m-, m.p. 126°, and -p-tolyllosazone, m.p. 189°, α , m.p. 172°, and - β -naphthoylosazone, m.p. 225°, -phenylmethyllosazone, m.p. 69—70°, and - α -phenylmethylhydrazone- β -3-nitrophenylhydrazone, m.p. 199°.

J. D. R.

Aromatic amines as catalysts for the dehydrogenation of glyceraldehyde. H. H. STRAIN (J. Amer. Chem. Soc., 1938, 60, 1268).—Aromatic amines catalyse formation of mixed CO-compounds from glyceraldehyde in presence of H-acceptors; with O_2 peroxides and coloured ppts. are formed. Intermol.

oxidation and reduction may be the cause of variations in the yield of AcCO_2H .

R. S. C.

Preparation of dl - $\alpha\beta$ -diacetoxyisobutaldehyde. J. W. E. GLATTFIELD and W. E. MOCHEL (J. Amer. Chem. Soc., 1938, 60, 1011—1014).—Reduction of Me , b.p. 89°/10 mm., Et , b.p. 95°/10 mm., Pr^a , b.p. 103°/10 mm., Bu^a , b.p. 113°/10 mm., and n -amyl $\alpha\beta$ -dihydroxyisobutyrate (I), b.p. 119°/10 mm., gave neither the aldehyde nor alcohol. However, $\text{OAc}\cdot\text{CH}_2\cdot\text{CHMe}(\text{OAc})\cdot\text{COCl}$ (prep. by AcCl in 25—30% yield from the acid, new m.p. 59°, b.p. 92—97°, with H_2 -PdO in C_6H_6 gives 74% of $\alpha\beta$ -diacetoxyisobutaldehyde, b.p. 104°/30 mm.; 0.1N-NaOH yields a solution of the $(\text{OH})_2$ -aldehyde, which with $\text{NHPh}\cdot\text{NH}_2$ and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ gives compounds, $\text{C}_{16}\text{H}_{18}\text{ON}_4$, m.p. 144° (corr.), and $\text{C}_{16}\text{H}_{16}\text{O}_5\text{N}_6$, m.p. 264° (corr.), possibly $\text{OH}\cdot\text{CMe}(\text{CH}\cdot\text{N}\cdot\text{NHAr})_2$. With AcCl at 50° (I) gives the diacetate, b.p. 124°/3 mm.

R. S. C.

Condensation of p -toluenesulphinic acid and its esters with acetone. C. L. ARCUS and J. KENYON (J.C.S., 1938, 684—685).— $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{H}$ and its esters condense with COMe_2 to yield p -tolyl- β -(β -methylpentan- δ -onyl)sulphone, m.p. 94° [semicarbazone, m.p. 173° (decomp.)], synthesised by condensing $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$ with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SOCl}$. Since no olefinic compounds are formed, the mechanism is probably not by exchange of carbonium cations but by rearrangement of the diacetyl p -toluenesulphinic acid first formed.

E. G. B.

Reduction of the carbonyl group in unsaturated ketones, and the interconversion of geometrical isomerides during such reduction. C. L. ARCUS and J. KENYON (J.C.S., 1938, 698—699).—Reduction $[\text{Al}(\text{OPr}^i)_3]$ of cis- , b.p. 80°/27 mm., and trans- , b.p. 61—63°/12 mm., n -butylideneacetone yields the same dl - α -methyl- γ - n -propyl alcohol, b.p. 66—67°/16 mm. (H phthalate, m.p. 67°; p -nitrobenzoate, m.p. 29.5°; p -xenylurethane, m.p. 87°), identified by catalytic reduction to dl -methyl- n -amylcarbinol, b.p. 64—65°/13 mm. This identity of products indicates that interconversion of geometrical isomerides occurs at the stage when the alcohols exist as Al oxides.

E. G. B.

Action of magnesium *tert*-butyl chloride on octyl laurate. Reaction of sodium salts of fatty acids with magnesium aryl halides and magnesium primary, *sec*-, and *tert*-alkyl halides. A. D. PETROV and E. B. SOKOLOVA (J. Gen. Chem. Russ., 1938, 8, 199—206).—*sec*-Octyl laurate, b.p. 170—185°/10 mm., and MgBu^tCl in boiling PhMe yield laurone, m.p. 69°. MgPhBr and $\text{Pr}^a\text{CO}_2\text{Na}$ in Et_2O yield COPhPr ; the sole product with Na heptoate, isovalerate, or palmitate was Ph_2 . The reactions: $\text{R}\cdot\text{CO}_2\text{Na} + \text{MgR}'\text{X} \rightarrow \text{CORR}'$ ($\text{R} = \text{Pr}^a, \text{Pr}^i, \text{C}_{11}\text{H}_{23}$; $\text{R}' = \text{Et}, \text{Bu}^a$; $\text{X} = \text{Cl}, \text{Br}$), and $\text{R}\cdot\text{CO}_2\text{Na} + \text{MgR}'\text{X} \rightarrow \text{COR}_2 + \text{Na}_2\text{CO}_3 + \text{MgR}'\text{X}$ ($\text{R} = \text{Me}, \text{Pr}^a$; $\text{R}' = \text{Pr}^i, \text{Bu}^t$), are described.

R. T.

Secondary reactions in the condensation of organo-magnesium compounds with aliphatic ketones. M. TUOT (Compt. rend., 1938, 206, 1019—1021).— COMe_2 , COMeEt , COMePr^i , COMeBu^i , COPr_2 , and COPr^i_2 are condensed with MgRBr ($\text{R} = \text{Et}, \text{Pr}, \text{Pr}^i, \text{Bu}, \text{Bu}^i$, and *iso*amyl) when, in addition to the

usual Grignard reaction, the following are observed: (a) MgRBr reacts with the enolic form of the ketone to give $\text{R}\cdot\text{C}(\text{OMgBr})\cdot\text{CH}_2 + \text{RH}$; (b) two mols. of the ketone couple to form a ketol which then reacts with 2MgRBr with the liberation of 2RH ; (c) the formation of a *sec.* alcohol with the liberation of an ethylenic hydrocarbon. (a) occurs with Me ketones and more particularly if MgRBr has an α - or β -*tert.* C. (c) occurs principally with COPr_2 ; the extent of the reaction depends on the stereochemical structure of the mols.

J. L. D.

Behaviour of acetoxime in deuterium oxide.

Stereochemistry of ketoximes. H. ERLÉNMEYER and H. M. WEBER (Helv. Chim. Acta, 1938, 21, 614—615).— $\text{CMe}_2\cdot\text{N}\cdot\text{OH}$ exchanges only 1 H (that of the $\text{N}\cdot\text{OH}$) in D_2O . Isomerisation of oximes thus does not proceed by way of $\text{CR}_2\cdot\text{CR}\cdot\text{NH}\cdot\text{OH}$.

R. S. C.

Influence of radicals on isomerisation of *tert.*- α -keto-alcohols. (Influence of ethyl radicals.)

II. A. M. CHALETZKI (J. Gen. Chem. Russ., 1938, 8, 225—232).— $\text{COBu}\cdot\text{CHEt}$ in H_2O , CaCO_3 , and Br yields δ -bromo- $\beta\beta$ -dimethyl- δ -ethylhexan- γ -one, b.p. 93—95°/12 mm., converted by boiling with KOAc in EtOH into δ -acetoxy- $\beta\beta$ -dimethyl- δ -ethylhexan- γ -one, b.p. 102—104°/14 mm., which is hydrolysed by 10% K_2CO_3 (2 days at 100°) to $\beta\beta$ -dimethyl- δ -ethylhexan- δ -ol- γ -one, b.p. 91—92°/11 mm.; a solution in EtOH of this when heated for 8 hr. at 120° with H_2SO_4 yields $\beta\beta$ -dimethyl- γ -ethylhexan- γ -ol- δ -one, b.p. 93°/10 mm. (semicarbazone, m.p. 204—205°). The keto-alcohol yields EtCO_2H and $\text{COEtBu}\cdot$ when oxidised with CrO_3 , and is reduced by Na in EtOH to $\text{CHEt}_2\cdot\text{CHBu}\cdot\text{OH}$.

R. T.

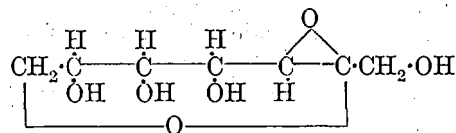
Halogenoalkylglucosides. I. Monohalogenoalkyl derivatives. II. Dihalogenoalkyl derivatives. H. W. COLES, (Miss) M. L. DODDS, and F. H. BERGEIM (J. Amer. Chem. Soc., 1938, 60, 1020—1022, 1167—1168).—I. $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{OH}$, glucose, and HCl gas give only a hygroscopic syrup, but $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{OH}$, acetobromoglucose, and Ag_2CO_3 give 45—50% of β -d- β -chloroethylglucoside tetra-acetate, m.p. 114°, $[\alpha]_D^{25} -21.25^\circ$ in COMe_2 . Similarly are obtained β -d- γ -chloropropyl-, m.p. 74°, $[\alpha]_D^{25} -12.25^\circ$, - β -bromoethyl-, m.p. 117.3°, $[\alpha]_D^{25} -20.5^\circ$ in COMe_2 , and - β -chloroisopropyl-glucoside tetra-acetate, m.p. 113°, β -d- β -chloroethylglucoside tetrabenzoate (obtained in poor yield), m.p. 59°, β -d- β -chloroethyl-, m.p. 137°, and - γ -chloropropyl-xyloside triacetate, m.p. 108.5—109°, β -d- β -chloroethyl-, m.p. 78—80°, - γ -chloropropyl-, m.p. 85°, and - β -chloroisopropyl-lactoside hepta-acetate, m.p. 95—97°, β -d- β -bromoethyl-, m.p. 111°, - β -chloroethyl-, m.p. 117°, and - γ -chloropropyl-galactoside tetra-acetate, m.p. 78°. M.p. are corr.

II. Dihalogenohydrins condense only with difficulty under the above conditions. β -d- $\beta\beta$ -Di-bromo-, m.p. 107.5°, and -chloro-isopropylglucoside tetra-acetate, m.p. 122—123°, and β -d-di-bromo-isopropylxyloside triacetate, m.p. 156—157°, are described. β -Benzobromoglucose and $\text{OH}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$ give an impure product. M.p. are corr.

R. S. C.

Structure of sedoheptulosan (anhydrosedoheptose). C. S. HUDSON (J. Amer. Chem. Soc., 1938, 60, 1241—1243).—The annexed structure fol-

lows for this sugar derivative from the oxidation of its Me_4 ether to trimethoxyriboglutamic acid and from



the identity of α -sedoheptitol with *D*- β -mannoheptitol. This agrees with its containing 1 $\text{CH}_2\cdot\text{OH}$, with the formation of a similar anhydro-derivative (formulated analogously as a *D*-altrosan) from *d*-altrose, and the non-formation of such an oxide from arabinose which cannot give a 7-membered ring. The ring structure of sedoheptulose remains in doubt.

R. S. C.

***d*- α , α -Galactose and its derivatives.** W. D. MACLAY, R. M. HANN, and C. S. HUDSON (J. Amer. Chem. Soc., 1938, 60, 1035—1040).—The amination of *d*- α , α -galactonic acid (prep. from *d*- α -galactose modified to give a 70% yield by way of the lactone, decomp. 219—220°, $[\alpha] +64.8^\circ \rightarrow +57.4^\circ$ in 2 days), m.p. 221° (decomp.), $[\alpha] +5.6^\circ$ (slowly mutarotates) (Na , $+2\text{H}_2\text{O}$, $[\alpha] +4.3^\circ$, Ca , $+9\text{H}_2\text{O}$, Cd , brucine , $+2.5\text{H}_2\text{O}$, m.p. 157—158°, $[\alpha] -18.8^\circ$, and quinine salts, m.p. 194°, $[\alpha] -102.2^\circ$), is proved by prep. from the lactone of the phenylhydrazide, m.p. 223—225°, $[\alpha] -19.3^\circ$, and *amide*, m.p. 228°, $[\alpha] -23.2^\circ$. With 2.5% Na-Hg the lactone gives α -*d*, α -galactose, $+ \text{H}_2\text{O}$, sinters at 103° (loss of H_2O), and anhyd., m.p. 167—169°, $[\alpha] -44.9^\circ \rightarrow -61.7^\circ$ in 370 min. (k increases with time), the configurative relationship of which to *l*-galactose is reflected in its properties and in those of its derivatives. Thus the octose yields a *hepta*-acetate, m.p. 88—90°, $[\alpha] -0.9^\circ$ in CHCl_3 (converted by H_2SO_4 in Ac_2O - AcOH into the oily β -*d*, α -galactose *hepta*-acetate, $[\alpha] -61.4^\circ$ in CHCl_3), with HCl-MeOH gives β -methyl-*d*, α -galactoside, m.p. 186—187°, $[\alpha] -147.7^\circ$ (*hexa*-acetate, m.p. 118.5—119°, $[\alpha] -90^\circ$ in CHCl_3), and a syrupy α -methylglucoside, $[\alpha]$ about $+2^\circ$ (*hexa*-acetate, m.p. 162°, $[\alpha] +16.8^\circ$ in CHCl_3), with H_2 -Raney Ni in H_2O at 98°/166 atm. gives *d*, α -galactitol, m.p. 130°, $[\alpha] -0.5^\circ$ in saturated aq. $\text{Na}_2\text{B}_4\text{O}_7$ (*octa*-acetate, m.p. 141°, $[\alpha] +40.4^\circ$ in CHCl_3), and gives a *benzylthiol* derivative, m.p. 208—209°, $[\alpha] +18.5^\circ$ in abs. $\text{C}_5\text{H}_5\text{N}$ (*hepta*-acetate, m.p. 88—89°, $[\alpha] -29.6^\circ$ in CHCl_3). M.p. are corr. $[\alpha]$ are $[\alpha]_D^{25}$ in H_2O unless otherwise stated. R. S. C.

Di-*p*-toluenesulphonation of β -methylcellobioside. α -Cellobiomethyllose. J. COMPTON (J. Amer. Chem. Soc., 1938, 60, 1203—1205).—In $\text{C}_5\text{H}_5\text{N}$ β -cellobioside with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, followed by Ac_2O , gives 67% of β -methylcellobioside *penta*-acetate 6:6'-*di-p*-toluenesulphonate, m.p. 161—162°, $[\alpha]_D^{25} -1.07^\circ$ in CHCl_3 , converted by NaI-COMe_2 into the 6:6'-*di*-iodide, m.p. 218—219°, which with Zn dust and a trace of H_2PtCl_6 in 75% AcOH at 80° gives β -methylcellobiomethylloside *penta*-acetate, m.p. 214—215°, $[\alpha]_D^{25} -35.2^\circ$ in CHCl_3 , converted by $\text{Ba}(\text{OMe})_2$ into β -methylcellobiomethylloside, m.p. 198—199°, $[\alpha]_D^{25} -29.8^\circ$ in H_2O , or by $\text{H}_2\text{SO}_4\text{-Ac}_2\text{O-AcOH}$ into α -cellobiomethyllose *hexa*-acetate (I), m.p. 236—237°, $[\alpha]_D^{25} +41.1^\circ$ in CHCl_3 . With NaOMe-MeOH (I) gives α -cellobiomethyllose, m.p. 205—206°, $[\alpha]_D^{25} +59^\circ \rightarrow$

+18.9° in 2 hr. in H₂O. (I) is hydrolysed by Ac₂O-AcOH-H₂SO₄ more slowly than are β-methylglucoside tetra-acetate, β-methylcellobioside hepta-acetate, and β-methylglucoside triacetate; of these four substances only (I) shows the complex nature of the reaction by irregularities in the reaction velocity.

R. S. C.

Emulsin. XXXIV. Fermentative fission of diglucosides of dihydric alcohols and phenols. B. HELFERICH, R. HILTMANN, and W. REISCHEL (Annalen, 1938, 534, 276—282).—The rate of hydrolysis of pyrocatechol-di- is about 1/10th that of the mono-glucoside but attains nearly the val. of the latter if the OH at C₆ of one sugar residue is converted into O-SO₂Me. The mono- and di-glucosides of protocatechualdehyde and the trans-cyclopentane-1:2-diols differ widely in their rates of enzymic hydrolysis but the introduction of the MeSO₂ group has a much smaller influence. The following compounds are described: *pyrocatechol-β-d-(1)-glucoside tetra-acetate β-d-(2)-glucoside triacetate 6-methanesulphonate*, m.p. 159—160°, [α]_D²⁰ -38.6° in CHCl₃ (from pyrocatechol-β-d-glucoside tetra-acetate, acetobromoglucose 6-methanesulphonate, and aq. NaOH at room temp.), hydrolysed (NaOMe in MeOH) to the amorphous glucoside; *protocatechualdehyde-β-d-(4)-glucoside tetra-acetate β-d-(5)-glucoside triacetate 6-methanesulphonate*, m.p. 183—184° (corr.), [α]_D²⁰ -62.3° in CHCl₃, and the corresponding Ac-free compound, decomp. >300°, [α]_D²⁰ -62.5° in H₂O; *1-trans-cyclopentane-1:2-diol-β-d-(1)-glucoside tetra-acetate β-d-(2)-glucoside triacetate 6-methanesulphonate*, m.p. 182.5—183.5°, [α]_D²⁰ -31.6° in CHCl₃, and the corresponding d-compound, m.p. 150—152°, [α]_D²⁰ -13.5°, whence *1-trans-cyclopentane-1:2-diol-β-d-(1)-glucoside-β-d-(2)-glucoside 6-methanesulphonate*, [α]_D¹⁹ -55.1° in H₂O, and the corresponding (l)-derivative, [α]_D¹⁹ -27° in H₂O.

H. W.

Verbenalin (verbenalloside) and verbenalol. J. CHEYMOL (Bull. Soc. chim., 1938, [v], 5, 633—642; cf. A., 1938, II, 127).—Verbenalloside (I) (cf. Reichert, A., 1935, 1041), C₁₇H₂₄O₁₀, m.p. 180°, [α]_D²⁴ -180.83° in H₂O, is reduced (Raney Ni) at room temp. and atm. pressure to a H₄-derivative, C₁₇H₂₈O₁₀. (I) is hydrolysed, by emulsin or careful use of H₂SO₄, to glucose and verbenalol, C₁₁H₁₄O₅, m.p. 140.5°, [α]_D²⁴ -29.22° in H₂O, which possesses a lactone, OMe, and CO groups, two labile H, and a double linking; it is probably linked to the glucose residue through the enolic OH. Physical consts. are recorded. (Cf. A., 1937, II, 7.)

A. T. P.

Derivatives of verbenalloside. J. CHEYMOL (Bull. Soc. chim., 1938, [v], 5, 642—653).—Verbenalloside [Ac₄ or Ac₅ derivative, m.p. 131°, [α]_D²⁰ -133.71° in EtOH (cf. A., 1937, II, 384; III, 333)] is hydrogenated (Pt-Ni in aq. EtOH) at room temp. and pressure to a H₄-derivative, m.p. 160—165° (cf. preceding abstract), hydrolysed by emulsin or H₂SO₄ to *tetrahydroverbenalol*, C₁₁H₁₈O₅. Verbenallosidic acid (verbenalinic acid), C₁₇H₂₆O₁₁, m.p. 210—212°, [α]_D²³ -185.99° in H₂O (Na, Ba salts), is hydrolysed to verbenalic acid. Absorption spectra are recorded.

A. T. P.

Colouring matter of Deccan hemp (*Hibiscus cannabinus*) flowers. Cannabiscitrin and canna-

biscetin. K. NEELAKANTAM and T. R. SESHADRI (Current Sci., 1938, 6, 504).—From the petals *cannabiscitrin*, C₂₁H₂₀O₁₃, is obtained, which yields a nona-acetate, and when hydrolysed gives *cannabiscetin*, a pentahydroxyflavonol differing from gossypetin, quercitagenin, and myricetin.

A. LI.

Acacipetalin from *Acacia stolonifera*, Burch.—See A., 1938, III, 632.

Recent results in the study of starch. M. SAMEC and M. BLINC (Kolloid-Beih., 1938, 47, 371—472).—A general review of published work.

F. L. U.

Structure of the products of periodic acid oxidation of starch and cellulose. E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1938, 60, 989—991).—The product obtained by oxidising maize starch or cotton with 1 mol. of HIO₄ gives, when hydrolysed by N-HCl at 100°, glyoxal (isolated as phenyl- or phenylbenzyl-osazone or, after Br-oxidation, as BaC₂O₄) and *d*-erythrose (isolated, after Br-oxidation, as the lactone or brucine salt of *d*-erythronic acid). Fission by HIO₄ is thus proved to occur between C₁₂ and C₁₃ of the C₆ units. Yields are low (15—33%) owing to destruction of material during hydrolysis, incomplete degradation of the polymeride, and, possibly, presence of other C₆ units in minor amounts.

R. S. C.

Highly polymerised compounds. CXCI. Constitution of wheat starch. H. STAUDINGER and E. HUSEMANN (Ber., 1938, 71, [B], 1057—1066).—Examination of wheat starch along the lines used for potato starch (A., 1936, 710; 1937, II, 87) shows that "starch" is not a chemical individual but a polymeric homologous series; this is true also of its derivatives. The differences in the sp. viscosities of the different starches depend therefore on the differing size of the macromols. and not on mol. aggregates. The relationships between degree of polymerisation and sp. viscosity show that the macromols. of the starches are constituted quite differently from those of the celluloses, which have unbranched thread mols.; the *K_m* consts. of the starches and their derivatives are $\frac{1}{5}$ — $\frac{1}{10}$ of those of the cellulose series. Since the viscosity of a solution is a measure of the length of the dissolved mol. the macromols. of the starches are much shorter than those of the celluloses of equal degree of polymerisation. Determinations of terminal groups contradict the assumption of a distorted mol. but are in harmony with the presence of short glucose chains the CHO groups of which are in glucosidic union with the OH of other short chains. Such a macromol. of a trimethylstarch yields relatively large amounts of tetramethylglucose when hydrolysed and the aldehydic groups of the short chains are masked by the glucosidic anion. The constitution of starch is represented by the previous formula (*loc. cit.*) but the exact nature of the branching is not yet explained.

H. W.

Problem of lignification. I. Formation of young, highly lignified cell walls. II. Xylan. W. VOSS, R. BAUER, and J. PEIRSCHKE (Annalen, 1938, 534, 95—135, 135—161).—I. In the hope of securing more homogeneous results by examining

lignified cells of uniform age instead of stem wood the shells of different species of plum and walnut have been examined for uronic acids, pentosans, MeOH, and OMe. After treatment with ClO_2 and NaOH the content of xylan (I) and cellulose (II) has been determined. It is concluded that, independently of the undecided chain length or degree of polymerisation, the individual chains of (II) in the solid state are grouped to bundles or micelles. For (I) a similar main valency chain or macromol. is considered. X-Ray examination of (I) or of (I) allied with (II) does not, however, give such definite evidence as would be expected from the closely similar structure of the two complex mols. with glucosidically-united pyran rings. Preps. of (II) containing (I) give a less definite X-ray diagram than does (II); this becomes better defined after removal of (I). This removal of sparingly sol xylan (III) is effected by aq. alkali of such concn. that a marked alteration of the structure or diagram of (II) does not occur. After removal of (I) the residual material has (II) : (I) = 3 : 1 or 2 : 1. This cannot be explained by assuming that the chains of (I) are regularly or irregularly distributed in the interior of the aggregates of the chains of (II) but that they are arranged as a layer around a bundle of (II). If (I) is uniformly distributed over the micelle surface of (II) the cross-section of a holocellulose mol. composed of (III) and (II) appears as a ring surrounded by a circle. The ratios (II) : (III) = 3 : 1 and 2 : 1 are the relationships of the surface of the inner ring to that of the exterior circle, whereby it is assumed that the anhydrides of glucose and xylose have the same vol. It is possible that the exterior layer of (III) is equally marked in all cases and that the difference in the composition of the "holocellulose" is due to the no. of chains of (II) grouped in the interior or that the no. of chains of (II) is const. and the differences are caused by the nos. of chains of (III) in the external sheath of (III). In the material examined the amount of freely sol. xylan (IV) is considerably < that of (III); it appears to belong to the group of intermicellar materials, mainly by reason of its variability in composition. The association of (IV) and (II) is regarded as due essentially to a peculiar "morphological structure" or "architecture" and not to an "ester-like union" of the components. The CO_2H content of the xylans agrees approx. with that observed by Schmidt, and support is given to the observation of the latter that part of the CO_2H is not free but originally involved in ester or lactone formation. It is not, however, possible to share the view that CO_2H is primarily responsible for chain formation since (IV) is richer than (III) in CO_2H and hence should be more adaptable to linking with other chains or forming stoichiometric compounds. Although the possibility of the formation of new main valency linkings between chains by ester bridges to a greater or less extent is not denied, it is not considered that such "linkings" can give rise to compounds. The question "compound or no compound" between (I) and (II) is of the same kind as that of the existence of a NaCl mol. in the rock-salt lattice. If the netting of long main valency chains with one another occurs through new ester bridges the process involves not only the immediate chains but also other chains pre-

united by ester bridges to one of the involved chains. The degree of direct and indirect union depends not only on the no. of the ester bridges but also in a very high degree on the chain length. With very long chains of two or more carbohydrate units relatively few ester bridges would suffice to cause an almost complete union and netting of a (I)-(II) complex by main valencies.

II. (III) is obtained from fruit stones by pptn. as an alkali xylan compound by addition of EtOH to the alkaline solution and decomp. of the product under EtOH by AcOH or $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. Alternatively the alkaline solution is neutralised, conc. by evaporation at $40^\circ/\text{vac.}$, and dialysed; then it is pptd. by EtOH and freed from ash by electrodialysis. $[\alpha]_D$ of the material in NaOH depends on the concn. of alkali, reaching a max. with the 2N solution. Since $[\alpha]_D$ of (I) from plum and cherry stones, walnuts, and beech stem wood and of their methylated products show close agreement it is considered that these xylans have identical structure as far as it is expressed in these properties. They also appear identical with the products from pine wood (Hess *et al.*, A., 1928, 1360), and maize seedlings (Link, B., 1929, 794) but not from esparto grass (Haworth *et al.*, A., 1935, 201). The homogeneity of specimens of (III) is indicated by the isolation of identical products from the same crude material in a series of experiments, by the constancy of $[\alpha]_D$ of portions obtained by fractional pptn. from a given source, and by the passage of a specimen through its $\text{Cu}\cdot\text{NH}_3$ compound without alteration of $[\alpha]_D$. The dependence of $[\alpha]_D$ on pretreatment is not a consequence of alcoholysis (compounds of $[\alpha]_D - 86^\circ$ have invariably been in long contact with EtOH). Since a product of lower can be transformed into one of higher $[\alpha]_D$ by dissolution in alkali and re-pptn. by aq. acid, the reverse transformation cannot be effected.

Hydrolysis of (III) with $\text{HCl}\cdot\text{MeOH}$ leads to the isolation of β -methyl-*d*-xyloside, after crystallisation of which *l*-arabinose (V) is detected in the residue as the *diphenylmethanedimethyldihydrazone*, m.p. 188° (decomp.). Polarimetric determination of xylose in the hydrolysate of (III) gives higher vals. than the reductometric method, the difference not being explicable by the presence of *d*-glucose, glucuronic acid, or glucuronolactone. The mean content of (V) in xylans of various origin is 10.7%, giving a ratio, xylose : (V) = 8 : 1. (III) obtained from cherry stones contains 16.5% of hexuronolactone (VI), measured by the CO_2 evolved on warming with acid. The val. is independent of the mode of prep. of (III) and is identical with that given by potentiometric titration. The identity of the lactone is not determined. It is regarded as present in the initial material and not as produced during the treatment with ClO_2 since the content after action of ClO_2 is never > that observed previously and, further, since (III) is not degraded by prolonged contact with ClO_2 . The structure of (III) differs in its nature from that of cellulose formed exclusively from *d*-glucose units. A sole participation of *d*-xylose units is out of the question but it remains undecided whether (V), (VI), OMe, and Ac are common to xylans from other sources.

Less is known of (IV) than of (III) and it is not yet

certain whether the isolated preps. show the same uniformity as those of (III). The content of (VI) in (IV) is $>$ that in (III) and consequently less furfuraldehyde is obtained by distillation according to Krüger-Tollens. (IV) is much more freely sol. than (III) in H_2O and $EtOH-H_2O$. $[\alpha]_D$ in aq. alkali are $<$ those of (III). Whether the displacements of $[\alpha]_D$ by the fractionation of preps. of (IV) is due to separation into differing portions or whether the manipulations lead to the establishment of an equilibrium connected with the lactone question of (III) remains undecided. Increase of $[\alpha]_D$ of (IV) by passage through a Cu-alkali complex to a val. approaching that of (III) is of interest particularly in connexion with the higher content of (V). H. W.

Problem of lignification. III. Fermentative fission of xylan. W. VOSS and G. BUTTER (Annalen, 1938, 534, 161—185).—The enzyme preps. are derived from germinating barley, the vineyard snail, and a material "Luizym." The substrates are the xylans obtained previously. The hexose content of freely sol. (I) and sparingly sol. (II) xylan, determined by fermentation of the hydrolysates, is 4%. Enzymic fission of the xylans is effected with their colloidal solutions, readily obtained by electrodialysis of their aq. alkaline solutions. The concn. is determined by the furfuraldehyde distillation (Krüger-Tollens) which gives low but comparative vals. Controllable differences are observed during the prep. of these solutions. Those of (I) and (II) obtained by Schmidt's method are transparent but gradually increase in viscosity when kept and ultimately set to clear gels. A solution of (I) obtained from the alkaline solution of cherry stones was somewhat opalescent and that of (II) was milky but transparent; solutions from plum kernels and beech stem wood were uniformly non-transparent. All retained their properties after long preservation. In the enzymic hydrolysis of (I) the origin is important whereas little significance is attached to the mode of prep. Marked differences in fission are observed according as the cellulose (III) : (I) ratio is 3 : 1 or 2 : 1. In the hydrolysis of (II) the degree of fission is independent of the mode of prep. This is particularly important in the case of a material with very lengthy exposure to ClO_2 , proving the non-incidence of a shortening of the chain or the production of fresh CO_2H groups. (II) is hydrolysed considerably more slowly and less extensively than (I), fission being roughly parallel with hexuronic acid content. With (II) from differing sources the same distinct subdivisions are not observed as with (I) but the ratios (III) : (II) = 3 : 1 or 2 : 1 are noticeable. The course of the hydrolyses is followed by determination of sugar (Bertrand). Admixture with other sugars, such as arabinose, or with hexuronic acid does not influence the calculation. The possible formation of di-, tri-, or higher saccharides is important but although evidence of their production has been obtained they do not accumulate in the solution. Preparatively xylose is the only sugar which has been detected and appreciable amounts of disaccharide are certainly not present; arabinose could not be isolated even with a suitable hydrazine (cf. preceding abstract). Hydrolysis of (II) leaves a residue which according to $[\alpha]_D$ is identical with the

initial material although the possibility of some degradation is not entirely excluded. With (I), in agreement with the very extensive hydrolysis, an unaffected material could not be isolated. Observations during the preparative hydrolysis of (I) and (II) and kinetic investigation of the course of fission indicate that in spite of intermediate phases the mechanism of the hydrolysis of all xylans is fundamentally the same and, conversely, that (I) and (II) have a common structural principle. H. W.

Problem of lignification. IV. Kinetics of the enzymic fission of xylan. W. VOSS and G. BUTTER (Annalen, 1938, 534, 185—204).—Enzymic hydrolysis of xylans occurs best at pH 4.65. Fission of freely sol. (I) and sparingly sol. (II) xylan, like that of starch, lichenin, and cellulose, is a sequence of changes; hydrolysis is not homogeneous but at any rate in the beginning is a micro-heterogeneous change. Nevertheless during a portion of its course the change appears to be unimol. if the enzyme concn. is low. Subsequently the progression of the coeff. indicates a restriction. With definite concn. of enzyme the Schütz rule is obeyed during a certain time. Restriction of the action is not due to the d -xylose formed. Equal degrees of hydrolysis are reached when the products of amount of enzyme and time of reaction are const. Under the influence of the Luizym enzyme the extent of the fission of (I) increases by 7% when the amount of enzyme is doubled or when time is doubled and amount of enzyme remains const.; this regularity is not observed with the snail enzyme. Corresponding observations are recorded with (II). H. W.

Problem of lignification. V. Composition of certain stem woods. W. VOSS and G. MELHURN (Annalen, 1938, 534, 204—209).—In the "model" wood of the cherry and plum kernel the ratio cellulose : sparingly sol. xylan (I) = 3 : 1 and 2 : 1, respectively. Examination of the stem wood of cherry, plum, and walnut shows the absence of a similar ratio. Extraction of the finely divided material with "solvent E13" removes amounts slightly $>$ those obtained from the kernels, but exhaustion with H_2O is practically unattainable. Calc. on the material treated with H_2O the OMe content is of the same order. The % of AcOH, pentosan, and lignin is $<$ in the kernels whereas that of cellulose is higher. The remarkably low content of freely sol. xylan or of the portion of the skeleton substance sol. in 0.2% NaOH is connected with the large proportion of material sol. in H_2O . Relationships appear complicated since in the Krüger-Tollens determination of plum stem wood 27.0% of pentosans are found by pptn. with phloroglucinol but only 19.1% by pptn. with barbituric acid (which should not react with hydroxymethylfurfuraldehyde). Apparently hexosans are present in considerable proportion. Further the latter vals. considerably exceed those obtained by extraction of the skeleton substance with 0.2% and 0.5% alkali. Large amounts of pentosans pass into solution during the treatment with ClO_2 . Simple relationships between (I) and Ac are not observed possibly owing to the presence of other polysaccharidic components. H. W.

Degradation of straw and red beechwood by sodium hypochlorite. R. S. HILPERT and G. HECHLER (Ber., 1938, 71, [B], 1066—1070).—Treatment of straw with 35% NaOH at 100° and of the residue with about 4% NaOCl followed by 16% NaOH at 70° gives a "cellulose" the composition of which is nearly that of a disaccharide. Further treatment with NaOCl causes no apparent change but half the residue dissolves when treated with alkali. The product darkens somewhat at >100°. The lignin and pentosan content is very low and OMe has declined from 4% to 0.5—1%. The composition is unaffected by repeated treatment with NaOCl and NaOH. The elementary composition of the product obtained in a similar manner from red beechwood corresponds with that of a triose but the OMe content is only slightly diminished (6% to 5%) whilst the lignin (I) yield (14%) is high and the pentoses are diminished from 24% in the wood to 4%. It is obvious therefore that (I) is a reaction product and not a component and, further, that OMe is in part united to hexoses which are resinified by acids. It appears unlikely that the products are formed by loss of H₂O from two carbohydrate residues since this involves the assumption of the presence of H₂O united by subsidiary valencies; the product from straw, however, dissolves in part in Schweitzer's reagent to a very viscous solution from which the dissolved substance is pptd. by acids; important differences in composition between residue and ppt. are not observed. H. W.

Cellulose hydrolysis by means of ethyl mercaptan. II. M. L. WOLFRAM, L. W. GEORGES, and J. C. SOWDEN (J. Amer. Chem. Soc., 1938, 60, 1026—1030; cf. A., 1937, II, 137).—Changes of $[\alpha]$ and η of 5% solutions of cellulose in HCl (d 1.2) are recorded. Products were recovered and treated with EtSH after varying times. Determinations of S and η in cuprammonium solution of the SET derivatives and of the regenerated SH-free products indicate a gradual decrease in the degree of polymerisation from 114 to 23; in the early stages, however, data calc. from η and S content do not agree. The Cu no. of the SET-derivatives was 1.8—5.5, that of the S-free products being 5—28.4. R. S. C.

Highly polymerised compounds. CLXXIX. Determinations of the mol. wt. of cellulose ethers. H. STAUDINGER and F. REINECKE (Annalen, 1938, 535, 47—100).—Mol. wt. determinations have been made of partly ethylated celluloses and their acetates, of ethylcellulose (I) in C₆H₆, and of the corresponding Me compounds. The investigation of the macromol. structure of cellulose (II) thus extends over the following changes: nitrates \leftarrow (II) \rightleftharpoons triacetates \rightleftharpoons cellite \rightarrow (I) and its acetates and methylcelluloses and their acetates. It is thus established that (II) and its derivatives can be converted into polymeric-analogous compounds if degradation of the sensitive macromols. by acids or by oxidation is avoided. In consequence of the magnitude of the macromols. the least trace of harmful reagents can cause profound degradation and inhibit a conversion into polymeric-analogous products. The polymeric-analogous transformations prove that for (II) and many of its derivatives the colloidal particles in the

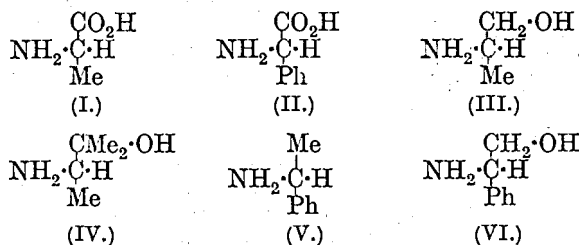
dil. solutions are the macromols. themselves. This proof is the more important since (I) in C₆H₆ is micellary. These associates differ in their structure from the micelles considered by Meyer and Mark as causative of the colloidal nature of solutions of (II) since these authors assume that the crystallites, the units of solid (II), pass unchanged into solution as micelles and cause the colloidal properties. Such micelles do not exist in solution and the colloidal phenomena of solutions of (II) are caused by the length of the macromols. Osmotic determinations of the mol. wt. establish the macromol. structure of the colloidal particles of all homopolar derivatives of (II). The proof of polymeric-analogous transformations is much more simply afforded by determinations of viscosity since the η_{sp}/c vals. of two series of polymeric-analogous compounds are in the ratio of their K_m vals.; these are recorded for many derivatives. The relationships between η and chain length are characteristic not only of macromol. compounds but also for simpler derivatives, e.g., of glucose or cellobiose, provided only that these have an extended form. The K_m consts. of complex derivatives cannot be calc. as accurately as those of the simpler, homogeneous materials since invariably mixtures of polymeric homologues are concerned. The vals. of K_m are valid for products which are reasonably homogeneous after fractionation. For unfractionated technical material the mean degree of polymerisation is greater when determined viscosimetrically than when determined by osmosis, and determinations of viscosity give only a rough approximation. In spite of large differences in the fundamental mol. wt. and in the structure of the products there is little difference between the known K_m consts. for fractionated celluloses and their derivatives and these are nearly independent of the solvent. The same relationships between η and degree of polymerisation in the region of sol solutions exist between all derivatives of (II) independent of the structure of their mols. The differences between the K_m consts. of different derivatives of (II) depend on differences in the degree of solvation of the macromols. in the different solvents. H. W.

Shape and size of methylcellulose molecules in solution.—See A., 1938, I, 357.

Preparation of *n*-dodecylamine and di-*n*-dodecylamine from dodecyl chloride and anhydrous liquid ammonia. J. P. WIBAUT, F. HEIERMAN, and H. M. WAGTENDONK (Rec. trav. chim., 1938, 57, 456—458).—*n*-C₁₂H₂₅Cl and liquid NH₃ at 75—80° in 72—90 hr. yield a mixture of *n*-dodecylamine, b.p. ~80°/0.7 mm., m.p. 26.2° (lit. 25°), and di-*n*-dodecylamine, b.p. 195°/0.7 mm., m.p. 44.4° (lit. 58°) (hydrochloride, m.p. 203—204°). J. D. R.

Configurative relationships between aromatic and aliphatic amines. H. REIHLEN, L. KNÖPFLE, and W. SÄPPER (Annalen, 1938, 534, 247—275).—The reference compound is *l*(+)-alanine (I) and correspondingly formula (II) is assigned to *l*(+)- α -aminophenylacetic acid. The arrangement of functional derivatives of the acid is self-explanatory. If the compound contains no CO₂H all substituents which have an O, N, or halogen atom near to the NH₂ independently of the no. of C are functional deriv-

atives of CO_2H . (III) and (IV) are therefore related to (II). If the asymmetric C carries two non-sub-



stituted hydrocarbon residues (or not substituted in the immediate vicinity) the arrangement is arbitrary as in (V). In such cases it is recommended to regard the smaller (or with an equal no. of C the more strongly branched or cyclic) hydrocarbon residue as if it replaced CO_2H . Hence (V) is *l*- α -phenylethylamine. *r*- β -Hydroxy- α -phenylethylamine is resolved into its optical antipodes by tartaric acid, whereby *d*(-)- β -hydroxy- α -phenylethylamine *H* *d*-tartrate (+1H₂O), m.p. 93°, $[\alpha]_D \pm 0^\circ$, and the corresponding hydrochloride, m.p. 169°, $[M]_D -37.9^\circ$ in H₂O, are obtained. The position of the alcohol in the *d*-series is established by its oxidation ($\text{KMnO}_4\text{-2N-H}_2\text{SO}_4$) to *d*(-)- α -aminophenylacetic acid in poor yield. *dl*- β -Bromo- α -phenylethylamine (VII) (hydrobromide, m.p. 187°) is obtained from the corresponding alcohol with PBr_3 and PBr_5 ; the action of these reagents or of $\text{PCl}_3 + \text{PCl}_5$ on the optically active alcohol is accompanied by racemisation; the reverse reaction is also impossible. Treatment of *dl*- β -chloro- α -phenylethylamine with *d*-tartaric acid in H₂O leads to *d*(-)- β -chloro- α -phenylethylammonium *H* *d*-tartrate, m.p. 173° (decomp.), $[M]_D +5.2^\circ$ in H₂O; the free base belongs to the *d*-series since its *Ac*, m.p. 134°, and *Bz*, m.p. 154°, derivatives have $[M]_D -246^\circ$, -234° , and -156° in EtOH, CHCl_3 , and COMe_2 and $[M]_D +51^\circ$ and $+17^\circ$ in EtOH and CHCl_3 respectively. *dl*-Acet- β -chloro- α -phenylethylamine has m.p. 105°. In acid solution the Cl is so unreactive that it cannot be replaced by H; in alkaline solution racemisation is very rapid. (VII) and malic acid in H₂O afford *l*(+)- β -bromo- α -phenylethylammonium *H* *l*-malate, $[M]_D -6.4^\circ$ in H₂O, whence ($\text{Ac}_2\text{O-NaHCO}_3$) acet-*l*(+)-bromo- α -phenylethylamine (VIII), m.p. 94°, $[M]_D +15.7^\circ$ in EtOAc (probably not optically homogeneous); the *r*-compound has m.p. 90°. H_2 (Pd-C in slightly acid solution) converts (VIII) into α -phenylethylamine (non-homogeneous), transformed into *l*(+)-*dibenzoyl*- α -phenylethylamine, m.p. 123°, $[M]_D +184^\circ$, $+198^\circ$, $+180^\circ$, $+260^\circ$, $+204^\circ$, $+217^\circ$, and $+210^\circ$ in MeOH, EtOH, COMe_2 , CHCl_3 , quinoline, $\text{C}_5\text{H}_5\text{N}$, and C_6H_6 respectively, thus establishing the configuration. Optically more stable compounds are obtained by hydrogenating (Pt-C in 2N-HCl at 60°/atm. pressure) the C_6H_6 ring, which is proved to occur without partial racemisation. Thus are obtained; *d*(-)-acet- α -cyclohexylethylamine, m.p. 122°, $[M]_D \pm 0^\circ$ in MeOH (for this and succeeding compounds the vals. of $[M]_D$ in EtOH, COMe_2 , CHCl_3 , and quinoline are usually also quoted); β -hydroxy- α -cyclohexylethylamine hydrochloride, m.p. 185—187°, $[M]_D -16.7^\circ$ in H₂O; *d*(+)-benz- β -hydroxy- α -cyclohexylethylamine, m.p. 170°, $[M]_D +173^\circ$ in $\text{C}_5\text{H}_5\text{N}$; *d*(+)-benz- β -

benzoyloxy- α -cyclohexylethylamine, m.p. 193.5—194.5°, $[M]_D +65^\circ$, $[M]_{546} +77^\circ$ in $\text{C}_5\text{H}_5\text{N}$; *d*(+)-benz- β -acetoxy- α -cyclohexylethylamine, m.p. 158°, $[M]_D +61^\circ$, $[M]_{546} +69^\circ$ in $\text{C}_5\text{H}_5\text{N}$; *d*(-)-*N*-dibenzoyl- β -benzoyloxy- α -cyclohexylethylamine, m.p. 117—119°, $[M]_D -503^\circ$, $[M]_{546} -578^\circ$ in $\text{C}_5\text{H}_5\text{N}$; *d*(-)-C-cyclohexylethylenediamine dihydrochloride, m.p. 255—260°; *d*-diacetyl-C-cyclohexylethylenediamine, m.p. 192°; *d*-dibenzoyl-C-cyclohexylethylenediamine, m.p. 187—188°. Comparison of $[M]_D$ in several solvents of a large no. of amine derivatives which differ from one another only according as they contain the Ph, cyclohexyl, or Pr^β group shows that in the aliphatic and alicyclic series the *l*-configuration in the aromatic series the *d*-configuration is present when the compound is strongly laevorotatory in quinoline and when in a N-free solvent the Ac derivative is much more strongly laevorotatory than the Bz compound. The first rule may be phrased: *l*-configuration is present when the replacement of Ph by cyclohexyl or any aliphatic group causes marked displacement of the rotatory power towards the left. The influence of optical superposition and of solvents is also discussed.

The following compounds are incidentally described: *d*(-)-, m.p. 118°, and *dl*-, m.p. 103°, -acet- β -acetoxy- α -phenylethylamine; *d*(+)-, m.p. 181°, and *dl*-, m.p. 153°, -benz- β -hydroxy- α -phenylethylamine; *d*(+)-benz- β -acetoxy- α -phenylethylamine, m.p. 158°; *dl*-, m.p. 154°; and *d*-, m.p. 159—160°, -benz- β -benzoyloxy- α -phenylethylamine; *dl*-*N*-dibenzoyl- β -benzoyloxy- α -phenylethylamine, m.p. 142°. H. W.

Methylglucosaminide: its structure, and the kinetics of its hydrolysis by acids. R. C. G. MOGGIDGE and A. NEUBERGER (J.C.S., 1938, 745—750).—Irvine, McNicoll, and Hynd's betaine structure for methylglucosaminide hydrochloride (I) (cf. J.C.S., 1911, 99, 250; 1912, 101, 1128) based on evolution of NH_2Me on distillation with alkali and its abnormal resistance to acid hydrolysis is improbable. Neither fact is incompatible with a normal glycosidic structure since (a) very drastic alkaline fusion is necessary and NH_2Me probably arises from interaction of CH_2O thus formed with NH_3 , and (b) resistance to hydrolysis is due to the positively charged NH_2 , situated α to the glycoside linking, repelling H^+ ions, which catalyse this reaction. This is confirmed by a kinetic study of the hydrolysis of (I) and of *N*-acetylmethylglucosaminide (II), m.p. 189°, $[\alpha]_D +105^\circ$, prepared from glucosamine penta-acetate (III) and from methylglucosaminide tetra-acetate (IV) by refluxing with MeOH-HCl . (IV) could not be obtained cryst. from bromoglucosamine tetra-acetate (V), decomp. on heating, $[\alpha]_D +118.2^\circ$, but was so obtained from (I) and Ac_2O . These methods of prep. indicate a glycosidic and not a betaine structure for (II). The hydrolysis curve shows that the glycoside linking of (II), which has no charged NH_2 adjacent, is hydrolysed at the normal rate for pyranosides. Comparison of hydrolysis consts. of charged and uncharged glycosides provides vals. for the distance between the charged group and the glycoside linking of the right order of magnitude. Inhibition of acid catalysis by the charged group therefore explains the abnormal stability of (I). It also explains the non-conversion of glucosamine into a

glycoside by MeOH-HCl and the difference in behaviour of (III) and (V) towards this reagent. Energies of activation of (I) and (II), calc. from the hydrolysis const., confirm their pyranoside ring structure.

E. G. B.

Preparation of citrulline by hydrolysis of arginine. S. W. Fox (J. Biol. Chem., 1938, 123, 687—690).—Arginine hydrochloride is refluxed with 2 mols. of 5.68N-NaOH for 3½ hr. and the cooled solution acidified with AcOH. After concn. in vac. EtOH is added to the residue to ppt. citrulline. The crude product is purified through the Cu salt and again pptd. with EtOH. It is optically inactive.

P. G. M.

Thiolcarbamic esters (S-alkylthiourethanes) and their conversion into halogenated alkylsulphonic acids. M. BATTEGAY and R. KREBS (Compt. rend., 1938, 206, 1262—1264; cf. A., 1938, II, 222).—The lower (Me to amyl) S-alkylthiocarbamates (I) with aq. alkali afford RSH, CO₂, and NH₃. In anhyd. EtOH, there is no reaction. (I) in solutions of p_H 3 are stable; stronger acids in H₂O or EtOH, or alkalis, decompose them. Suspensions of (I) in H₂O at <10° with aq. Cl₂ or Br afford the corresponding alkylsulphonyl halide. *n*-Propylsulphonyl bromide, b.p. 89—90°/12 mm. (amide, m.p. 52°), is described.

J. L. D.

Labile sulphur in proteins. Action of alkalis on cystine and its derivatives. A. SCHÖBERL and T. HORNING (Annalen, 1938, 534, 210—225).—Determinations have been made of H₂S, NH₃, SH compounds (iodometrically and colorimetrically), elementary S, unchanged disulphide, total N, and NH₂-N in the products of the action of dil. NaOH on cystine (I) and its derivatives. (I) gives unchanged material, very much cysteine, little NH₃ and H₂S, and no S. Among other disulphides the amounts of NH₃ and H₂S are considerably greater and are usually equiv. to one another. Much NH₃ is obtained, particularly from diformylcystine (II), cystinyldiglycine (III), and SS-glutathione (IV) and much H₂S from cystine-hydantoin (V), (IV), diglycylcystine (VI), and dicarbobenzyloxycystinyldiglycine (VII). Iodometric and colorimetric determinations of SH compounds gave concordant results in only three cases. The amount of SH compounds obtained from (III) is comparable with that derived from (I). (V), (VII), and (IV) do not afford SH compounds but yield considerable amounts of S, also derived from (II) and dialanylcystine. AcCO₂H and (I) are isolated from (II). For (I) and its derivatives the primary hydrolysis appear to occur $[\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{S}]_2 + \text{H}_2 \rightleftharpoons \text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{SH} + \text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{S}\cdot\text{OH}$ but the change is not so well defined as with the α -disulphidocarboxylic acids (VIII) and appears to lead to an equilibrium. (I) and its derivatives are generally more stable than (VIII) towards alkali; (I) is very stable and is followed by (VII). Generally substitution in the NH₂ in the RCO residue diminishes the stability towards alkali, but the nature of the residue is very important. RCO induces great lability. (III) and (VI) are extensively hydrolysed with little side reaction. The influence of sequence of components is proved by comparison of the behaviour of (III) and (VI). (V)

I (A., II.)

gives about 50% of H₂S and 50% of S and consequently no SH compound; the change is probably $(\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{S})_2 = 2\text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{CH}_2 + \text{H}_2\text{S} + \text{S}$ and the methylenehydantoin yields CO(NH)₂ and AcCO₂H. (IV) is less stable towards alkali than any other cystine derivative except (V). It gives 68.8% of H₂S, 14.6% of S, and no SH compounds and is thus very closely resembled by (VII). The ready decomposability of these compounds is attributed to the structural position of the residue of (I) in the middle of the chain so that neither NH₂ nor CO₂H of (I) remains free.

H. W.

Hydrazides of higher unsaturated acids. IV. Hydrazide of stearolic acid, and its derivatives. A. OSKERKO (J. Gen. Chem. Russ., 1938, 8, 334—340).—*Et stearolate*, b.p. 195—197°/3 mm., and N₂H₄·H₂O in boiling Et₂O yield *stearolyldiazine*, m.p. 75—75.5° (hydrochloride, decomp. 126—132°; *N*-Ac derivative, m.p. 111—112°; compound with COMe₂, m.p. 104—105°), converted by I in aq. EtOH into *s-distearolyldiazine*, m.p. 122—123°.

R. T.

Bromine value of unsaturated nitriles. R. DELABY and J. HUBERT (Compt. rend., 1938, 206, 1120—1122; cf. A., 1931, 205).—The rate of Br absorption of $\beta\gamma$ -unsaturated nitriles CHR:CH·CH₂·CN (cf. A., 1937, II, 90) is inversely \propto to mol. wt. but is < that of the nitriles CH₂:CH·CHR·CN. For *trans*- Δ^8 -octenonitrile (I), b.p. 93—95°/20 mm., the rate of absorption \propto temp. and rises with increasing time and [Br]. The action of CuCN on a mixture of CHBu:CH·CH₂Br (80%) and CH₂:CH·CHBuBr yields a mixture, b.p. 84—89°/20 mm., of (I) and CH₂:CH·CHBu·CN. The Br absorption of this and of (I) indicates 16% of the *sec.* compound.

E. G. B.

Synthesis of phosphatides. II. Synthesis of α -kephalin distearate. III. Synthesis of natural lysolecithin. I. KABASHIMA (Ber., 1938, 71, [B], 1071—1073, 1073—1076; cf. A., 1938, II, 81).—II. Ba α -glycerophosphate is transformed by stearoyl chloride and Ba(OH)₂ into *Ba distearoyl- α -glycerophosphate* and thence into the *Ag* salt, which with bromocolamine picrate yields α -kephalin distearate, m.p. 175°, identical with that derived from the human brain. MeI in MeOH-C₆H₆ at 100—120° converts it into (?) α -kephalin trimethylammonium iodide. Treatment of it with pancreatin or snake venom does not lead to hæmolytically active products.

III. α -Monopalmitin is converted by POCl₃ in quinoline-CHCl₃ followed by H₂O into α -palmitoylglycerol- α' -phosphoric acid, the *Ag* salt of which is converted by bromocholine picrate in CHCl₃-COMe₂ at 100° into lysolecithin, which softens at 109°, becomes transparent at 130—150° and cloudy at about 200°, then gives a clear brown melt at 260° and decomposes at 262°. Its hæmolytic power is somewhat < that of the natural product from egg yolk.

H. W.

Double formula of organo-magnesium compounds. J. DÉCOMBE and C. DUVAL (Compt. rend., 1938, 206, 1024—1026; cf. A., 1936, 743).—MeI in EtOAc containing a Zn-Mg alloy (Mg:Zn = 1:1) and a trace of I at 60—70° affords a complex, $\text{Mg}[\text{ZnMe}_2\text{I}_2(\text{EtOAc})_2]$ (I), electrolysis of which in

EtOAc shows that Zn passes to the anode and Mg to the cathode. (I) with H_2O affords CH_4 , ZnI_2 , and MgI_2 . (I) (3.25 mols.) with BzCl (1 mol.) affords COPhMe (which indicates that it acts as an organo-Zn compound), a little EtOBz , and a compound containing Zn but no Mg, hydrolysed (cold dil. H_2SO_4) to an oil which with NaNO_2 -AcOH gives Et α -oximinobenzoyl-acetate. J. L. D.

Preparation and resolution of complex oxalato-compounds of gallium.—See A., 1938, I, 367.

Hydroxy-iodo-compounds of tin dialkyls. T. KARANTASSIS and C. VASSILIADIS (Compt. rend., 1938, 206, 842—844).—Prolonged interaction of SnR_2I_2 (R = alkyl) (2 mols.) with aromatic or heterocyclic bases (3 mols.) in EtOH at room temp. affords compounds SnR_2O , $\text{SnR}_2\text{I}\cdot\text{OH}$, probably formed by hydrolysis of the compounds $\text{SnR}_2\text{I}_2 + 2$ base described previously (cf. A., 1937, II, 450). Compounds in which R = Me, Et, m.p. 140—141°, Pr^B, m.p. 187°, Bu^B, m.p. >215°, and isoamyl are prepared. The isoamyl derivative is decomposed in air. J. L. D.

Synthesis in organic chemistry. J. VAN ALPHEN (Chem. Weekblad, 1938, 35, 390—398).—A review especially of researches carried out in Leiden. The following is new: (a) Na and a large excess of $\omega\omega'$ -dihalogenoparaffins ($>\text{C}_3$) give only cycloparaffins; (b) di-p-anisylketen can be prepared from α -chlorodi-p-anisylacetyl chloride by Staudinger's method. S. C.

Multiplanar configuration of the methylcyclohexane ring. A. I. VOGEL (Chem. and Ind., 1938, 541—542).—When dehydrated by P_2O_5 and then hydrogenated (PtO_2), 1-, 3-, and 4-methylcyclohexanol yield the same methylcyclohexane, but the 2-Me isomeride gives a product which has different *d* and *n* but becomes more normal when heated at 40—60° or kept. The products are considered to be boat and chair forms. R. S. C.

Oxidation of substituted cyclohexenes by selenious oxide. A. GUILLEMONAT (Compt. rend., 1938, 206, 1126—1128).—Oxidation of 1:6-dimethyl- Δ^1 -cyclohexene by SeO_2 , AcOH, and Ac_2O gives o-xylene and 2:3-dimethyl- $\Delta^{1,3}$ -cyclohexadiene, probably by the initial formation of the 6-OH-derivative (I). 1:2-Dimethyl- Δ^1 -cyclohexene gives the same products, probably by transformation of the intermediate 2-OH-derivative into (I), as indicated by the similar oxidation of 6- and 5-methyl- Δ^1 -cyclohexene to mixtures of 6- and 4- and of 4-, 5-, and 6-methyl- Δ^1 -cyclohexenyl acetate respectively. This transformation probably occurs when the intermediate Se compounds decompose. E. G. B.

Relationship between density distribution of certain valency electrons (*B*-electrons) and reactivity in aromatic hydrocarbons.—See A., 1938, I, 298.

Complex formation between polynitro-compounds and aromatic hydrocarbons. IV. Interaction of trinitromesitylene and trichlorotritrobenzene with hexamethylbenzene and with naphthalene. D. L. HAMMICK and A. HELICAR. V. Effect of methylation on the stability of tetranitromethane complexes. T. T. DAVIES and

D. L. HAMMICK (J.C.S., 1938, 761—763, 763—766; cf. A., 1935, 828).—IV. The effect of Me groups on the stability of complexes of polynitro-compounds with aromatic hydrocarbons is shown by the behaviour of the two-component systems of $\text{C}_6\text{Me}_3(\text{NO}_2)_3$ (I) and $\text{C}_6\text{Cl}_3(\text{NO}_2)_3$ (II) with C_6Me_6 and C_{10}H_8 , where in each case (a) the effect of nuclear H is eliminated, (b) the steric effect of substituents is approx. the same, and (c) their mesomeric effect on the nucleus is in the same sense. Temp.-composition curves for the four systems show that (II) forms stable solid complexes with the hydrocarbons whereas (I) does not. The liquid phases are yellow and colourless, respectively. This result can be due only to the positive inductive effect of Me making it electron-repelling, whereas Cl is electron-attracting. Greater reactivity of (II) with ethylenic substances results.

V. Stabilities of the coloured complexes of $\text{C}(\text{NO}_2)_4$ with aromatic hydrocarbons are compared by measurements of the rate of increase of colour of solutions of $\text{C}(\text{NO}_2)_4$ in CCl_4 as more hydrocarbon is added (cf. A., 1936, 1453). Results show that (a) stability increases with the no. of nuclear Me; (b) increase in the no. of side-chain Me does not progressively increase stability, which rises up to PhEt, falls with PhPr^B, and rises again with PhBu^v; (c) successive introduction of Ph groups into the side-chain of PhMe increases stability. (a) is related to the positive inductive effect of Me. E. G. B.

Nitration of phenylnitromethane. T. URBAŃSKI and (in part) J. GIEDRÓY (Compt. rend., 1938, 206, 1122—1124).—Nitration of $\text{CH}_2\text{Ph}\cdot\text{NO}_2$ by HNO_3 (*d* 1.5 or 80%) yields *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, m.p. 91°, and by 1:1 HNO_3 -oleum; 3:5-dinitrophenylnitromethane, m.p. 130°, decomp. 200°, oxidised (dil. HNO_3) to 3:5-(NO_2)₂ $\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$. It forms metallic salts and has explosive properties similar to those of α -trinitrotoluene. E. G. B.

Acceleration of the polymerisation of styrene by benzoyl peroxide.—See A., 1938, I, 363.

Thermal polymerisation of styrene in carbon tetrachloride. J. W. BREITENBACH, A. SPRINGER, and E. ABRAHAMCZIK (Österr. Chem.-Ztg., 1938, 41, 182—183; cf. A., 1938, I, 256).—The polymerisation of 0.5M and M solutions of styrene in CCl_4 at 140° gives products the mol. wts. of which, determined cryoscopically in dibromocamphane, are approx. 580 and 900, respectively. The Cl content of the product indicates that an equimol. additive product is formed between the polymeride and CCl_4 . J. W. S.

Synthesis of β -di-p-tert.-butylphenyl- β -dimethylbutane. WALTHER (J. Pharm. Chim., 1938, [viii], 27, 476—479).—p-tert.-Butylacetophenone (semicarbazone, m.p. 219°) with MgMeI (2.5 mols.) yields p-tert.-butylphenyldimethylcarbinol, m.p. 76°, which, treated successively with HBr in AcOH and Zn in AcOH, yields β -di-p-tert.-butylphenyl- β -dimethylbutane, m.p. 225°. J. D. R.

Phenyldodecane. A. D. PETROV and LAPTEVA (J. Gen. Chem. Russ., 1938, 8, 207).—Laurophenone is reduced by Clemmensen's method to α -phenyldodecane, b.p. 179—180°/13 mm., m.p. -7°. R. T.

Attempted photo-oxidation in the phenanthrene and naphthalene series. C. DUFRAISSE and R. PRIOU (Bull. Soc. chim., 1938, [v], 5, 611—626).—The following compounds do not form photo-oxides even in strong sunlight: phenanthrene and its 9:10- Ph_2 derivative; 1:4:2- $\text{C}_{10}\text{H}_5\text{Ph}_2\text{CHO}$, - $\text{C}_{10}\text{H}_5\text{Ph}_2\text{CO}_2\text{H}$, m.p. 226—227°, - $\text{C}_{10}\text{H}_5\text{Ph}_2\text{CO}_2\text{Me}$, 1:4:2:3- $\text{C}_{10}\text{H}_4\text{Ph}_2(\text{CO}_2\text{Me})_2$, m.p. 202—203°, and - $\text{C}_{10}\text{H}_4\text{Ph}_2(\text{CO})_2\text{O}$; 1:2:3:4-dibenzoylenaphthalene, m.p. 305—306°. Structural considerations for photo-oxidisability, and absorption spectra, are recorded.

A. T. P.

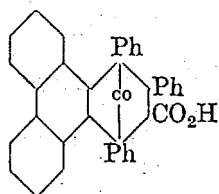
1-Methyl-2-n-propylphenanthrene. G. A. R. KON, E. S. NARRACOTT, and C. REID (J.C.S., 1938, 778).—Condensation of $\text{CHPr}^a(\text{CO}_2\text{Et})_2$ with β -1-naphthylethyl bromide yields β -1-naphthylethyl-n-propylmalonic acid, m.p. 173° (decomp.) (Et ester, b.p. 203—211°/2.5 mm.), decarboxylated to γ -1-naphthyl- α -n-propylbutyric acid, m.p. 68—69°. The chloride of this is cyclised ($\text{AlCl}_3\text{--CS}_2$) to 1-keto-2-n-propyl-1:2:3:4-tetrahydrophenanthrene, m.p. 53°, b.p. 206—208°/5 mm., giving with MgMeI a carbinol, dehydrated to 1-methyl-2-n-propyl-3:4-dihydrophenanthrene, b.p. 208—210°/13 mm., which is reduced (Pd-C) to 1-methyl-2-n-propylphenanthrene, m.p. 54° [picrate, m.p. 97°; styphnate, m.p. 118—119°; $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 112°; $s\text{-C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ derivative, m.p. 82—83°].

E. G. B.

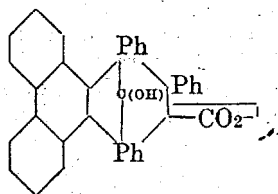
Attempted photo-oxidation in the mesodianthranyl series. C. DUFRAISSE, L. VELLUS, and (MME.) L. VELLUS (Bull. Soc. chim., 1938, [v], 5, 600—610; cf. A., 1937, II, 374).—9:9'-Dianthranyl, new m.p. 319—320°, and its 10:10'- Ph_2 derivative, m.p. 390—391° (anhyd. or +2PhMe), do not absorb O_2 when insolated in Et_2O , CS_2 , or C_6H_6 , nor do they react with maleic anhydride on fusion or in xylene. Theoretical considerations are discussed and absorption spectra are recorded.

A. T. P.

Highly-arylated aromatic compounds. VI. W. DILTHEY, S. HENKELS, and A. SCHAEFER (Ber., 1938, 71, [B], 974—979; cf. A., 1935, 967).—Diphenyldiphenylenecyclopentadienone (I) and CPh:CH at 100° yield CO and 1:2:4-triphenyl-5:6-diphenylenebenzene, m.p. 250°; the intermediate CO-compound could not be isolated. At 180° (I) and toluene yield 1:2:3:4-tetraphenyl-5:6-*oo'*-diphenylenebenzene, m.p. 292—293°, which could not be derived from tetracyclone and phenanthrene; the endocarbonyl compound could not be isolated. In boiling C_6H_6 (I) and $\text{CPh:C-CO}_2\text{H}$ unite without evolution of CO to the adduct (A or B), m.p. between 206° and 212° (much decomp.) according to the manner of heating; which does not dissolve in alkali; it passes



(A.)



(B.)

when heated into 2:3:6-triphenyl-4:5-*oo'*-diphenylenebenzoic acid, m.p. 314—315° [also obtained directly

from (I) and $\text{CPh:C-CO}_2\text{H}$ at 150—170°], which is readily sol. in alkali. Acecyclohexene (II) and C_2H_2 in molten phenanthrene give 2:5-diphenyl-3:4-1':8'-naphthylenebenzene, m.p. 162—163°, also obtained by distilling 2:5-diphenyl-3:4-1':8'-naphthylene-phthalic anhydride with soda-lime. CPh:CH and (II) at 250—300° afford 2:5:6-triphenyl-3:4-1':8'-naphthylenebenzene, m.p. 195—196°. Toluene and (II) at 250—270° afford 1:2:5:6-tetraphenyl-3:4-1':8'-naphthylenebenzene, m.p. 314°, also derived from tetracyclone and acenaphthylene (III) at about 250°. 2:5-Diphenyl-3:4-1:6-di-1':8'-naphthylenebenzene, m.p. 403°, is obtained from (II) and (III) at 250—300°.

H. W.

Synthesis of 9:10-dimethyl-1:2-benzanthracene. M. S. NEWMAN (J. Amer. Chem. Soc., 1938, 60, 1141—1142).— $\text{o-CO}_2\text{H-C}_6\text{H}_4\text{-CHMe-C}_{10}\text{H}_7\text{-}\alpha$ with a little ZnCl_2 in $\text{AcOH-Ac}_2\text{O}$ gives 50% of 10-acetoxy-9-methyl-1:2-benzanthracene, m.p. 192.4—193.4°, converted by MgMeBr into the oily anthrone, which when treated with more MgMeBr and heated at 240—250° gives 9:10-dimethyl-1:2-benzanthracene (32%), m.p. 122.4—122.8° (dipicrate, m.p. about 103—106°).

R. S. C.

Fused carbon rings. XIV. Synthesis of dicyclic compounds with an angular methyl group from substances containing a *n*-pentenyl side chain. G. H. ELLIOTT and R. P. LINSTEAD. **XV. Synthesis of derivatives of 8-methylhydrindane and of perhydroanthracene from substances containing a *n*-butenyl side chain.** K. D. ERRINGTON and R. P. LINSTEAD (J.C.S., 1938, 660—665, 666—672).—XIV. 2-Methylcyclohexanone, Δ^8 -*n*-pentenyl bromide, and Mg in Et_2O yield 2-methyl-1- Δ^8 -*n*-pentenylcyclohexanol (I), b.p. 122—124°/13 mm. Oxidation ($\text{Na}_2\text{CO}_3\text{--KMnO}_4$) of (I), followed by dehydration ($\text{H}_2\text{C}_2\text{O}_4$), yields γ -(2-methyl- Δ^1 -cyclohexenyl)butyric acid, m.p. 44°, together with the spiro-lactone of γ -(1-hydroxy-2-methylcyclohexyl)butyric acid, b.p. 135°/1.5 mm. The lactone when esterified ($\text{EtOH-H}_2\text{SO}_4$), dehydrated (SOCl_2 and $\text{C}_5\text{H}_5\text{N}$ in Et_2O), and hydrolysed yields the former acid, which when cyclised and reduced (cf. A., 1937, 292) affords 9-methyl-1-decahydronaphthalone [reduction ($\text{AlCl}_3\text{--cyclohexane}$) of the intermediate chloroketone giving a small amount of a different 9-methyl-1-octahydronaphthalone (semicarbazone, m.p. 228°)]. Reduction of this with $\text{Al(OPr}^i)_3$ and Pr^iOH gives (? *ois*)-9-methyl-1-decahydronaphthol, b.p. 134—135°/20 mm. Oxidation (conc. HNO_3) of the latter or ($\text{Ac}_2\text{O-conc. HNO}_3$) of the methyldecahydronaphthalone yields an acid which with Ba(OH)_2 gives (? *cis*)-8-methyl-1-hydrindanone. Cyclisation of (I) with $\text{Ac}_2\text{O-AcOH-H}_2\text{SO}_4$ yields an olefine, b.p. 98—103°/12 mm., and an alcohol (? 1:9-dimethyl-2- or -3-decahydronaphthol), b.p. 152°/17 mm., oxidised (CrO_3) to a ketone, $\text{C}_{12}\text{H}_{20}\text{O}$, b.p. 138.5°/13 mm. (semicarbazone, m.p. 223°). Dehydration (KHSO_4) of the alcohol affords an olefine, $\text{C}_{12}\text{H}_{20}$ (? 1:9-dimethyl- Δ^2 -octahydronaphthalene), b.p. 95—99°/10 mm., very similar to the above olefine, oxidised (KMnO_4) to a dibasic acid, $\text{C}_{12}\text{H}_{20}\text{O}_4$, m.p. 156° (also obtained by oxidation of the ketone, $\text{C}_{12}\text{H}_{20}\text{O}$). Further degradation results in a ketone, $\text{C}_{11}\text{H}_{18}\text{O}$ (? 1:8-dimethyl-2-hydrindanone),

b.p. 114°/9 mm. (*semicarbazone*, m.p. 214.5°), and a dibasic acid, $C_{11}H_{18}O_4$, m.p. 144°, differing from 2-methylcyclohexane-1:1-diacetic acid. The olefine $C_{12}H_{20}$ evolves no H_2 when heated with active Pt, and therefore contains a quaternary C, but with Pd-asbestos at 335° yields dimethylnaphthalene(s) (picrate, m.p. 134—135°), whilst the ketone $C_{12}H_{20}O$ with Pd-charcoal gives a trace of a phenol, m.p. 92—96° (picrate, m.p. 140—148°).

1:1-Dimethyl- Δ^5 -*n*-pentenylcarbinol is prepared from Δ^5 -*n*-pentenyl bromide, Mg, and $COMe_2$ in Et_2O (cf. A., 1936, 713).

XV. (a) 2-Methyl-1- Δ^7 -butenylcyclopentanol, b.p. 87—91°/10 mm. (from 2-methylcyclopentanone, Mg, and Δ^7 -butenyl bromide in Et_2O), yields with $H_2C_2O_4$ at 150° the (? Δ^1 -)cyclopentene, b.p. 168—169°; with P_2O_5 and H_3PO_4 at 150°, 8-methyl-(? Δ^5 -)hexahydroindene, b.p. 175—176°/761 mm. [very similar to that produced by dehydrating ($KHSO_4$) 8-methyl-6-hydrindanol]; and with Ac_2O -AcOH-conc. H_2SO_4 , an acetate hydrolysed to cis-8-methyl-6-hydrindanol, m.p. 66°, together with an isomeride, b.p. 112—113°/11 mm. Either isomeride with CrO_3 -AcOH yields the same hydrindanone (*semicarbazone*, m.p. 210°) identified by reduction (Clemmensen) to cis-8-methyl-hydrindane. Oxidation (conc. HNO_3) of the solid alcohol gives cis-1-methylcyclopentane-1:2-diacetic acid (? or the 1-carboxylic-2- β -propionic acid), m.p. 103° (also obtained from 8-methylhexahydroindene and $KMnO_4$), which with $Ba(OH)_2$ yields cis-7-methyldicyclo-[0:3:3]-octan-(? 2)-one, m.p. 26° (*semicarbazone*, m.p. 178°), oxidised by HNO_3 to cis-1-methylcyclopentane-1-carboxylic-2-acetic acid, m.p. 110°. (b) Et 2-methylcyclopentanone-2-carboxylate, when condensed with $CHBr\cdot CO_2Et$ and Mg in C_6H_6 , dehydrated ($KHSO_4$), and reduced (Adams catalyst), yields the *Et* ester, b.p. 140°/5 mm., of the above *cis*-acid, but when condensed with $CN\cdot CH_2\cdot CO_2Et$ in $C_6H_{11}N$ at 65°/5000 atm. gives *Et* 2-methylcyclopentylidene-1-cyanoacetate-2-carboxylate, b.p. 152—158°/1 mm., reduced (Al-Hg) and hydrolysed to the trans-1-methyl-1-carboxylic-2-acetic acid, m.p. 139°. (c) trans-2-Decahydronaphthalone with Δ^7 -butenyl bromide and Mg in Et_2O yields trans-2- Δ^7 -*n*-butenyl-2-decahydronaphthol, m.p. 39°, cyclised (Ac_2O -AcOH-conc. H_2SO_4) to the ester of trans-cis-2-perhydroanthrol, m.p. 145°. P_2O_5 at 150° converts this into dodecahydroanthracene, which yields anthracene with Pd-charcoal at 320°. (d) trans-Hydrindane gives indane with Pt-asbestos or Pd-charcoal at 310°. 8-Methylhydrindane and 8-methylhexahydroindene are unaffected by Pt, but with Pd at 330° yield indane.

A. Li.

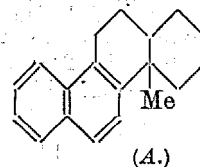
Synthesis of 9:10-dimethyl-, 9:10-diethyl-, and 5:9:10-trimethyl-1:2-benzanthracene. W. E. BACHMANN and J. M. CHERMIDA (J. Amer. Chem. Soc., 1938, 60, 1023—1026).—9:10-Dihydroxy-9:10-dimethyl-9:10-dihydro-1:2-benzanthracene with Zn-AcOH or HI does not give 9:10-dimethylan-thracene (I), but with H_2SO_4 -MeOH yields the Me_2 ether (II), m.p. 173.5—174.5°. With 45% Na-Hg this gives the Na_2 derivative, which is converted by MeOH into 9:10-dimethyl-9:10-dihydro-1:2-benzanthracene, an oil, dehydrogenated by S at 200° to (I). (I), m.p. 122—123° (mono-, m.p.

112.5—113°, and *di-picrate*, m.p. 102—106° after sintering at about 95°), is best (96%) obtained from (II) by Na or K in C_6H_6 - Et_2O . 9:10-Dimethoxy-9:10-diethyl-9:10-dihydro-, m.p. 172—173°, and 9:10-diethyl-1:2-benzanthracene (III), m.p. 98.5—99.5° (*picrate*, m.p. 97—98.5°), are similarly obtained. 5-Methyl-1:2-benzanthraquinone and $MgMeI$ give 9:10-dihydroxy-5:9:10-trimethyl-9:10-dihydro-1:2-benzanthracene, m.p. 204—206°, and thence by H_2SO_4 -MeOH- C_6H_6 the Me_2 ether, m.p. 228—229°, which with Na yields 5:9:10-trimethyl-1:2-benzanthracene (IV), m.p. 127—128°. (I), (III), and (IV) with $(CH\cdot CO)_2O$ give adducts, m.p. 238—240° (decomp.), 215—217° after sintering, and 250° after decomp., respectively, the ease of reaction being (I), (IV), >(III), anthracene >1:2-benzanthracene. R. S. C.

Photochemical transformation of $\Delta^{2,4}$ -cholestadiene. A. BUTENANDT and H. KUDSSUS (Z. physiol. Chem., 1938, 253, I—III; cf. A., 1937, II, 289; 1938, II, 226).—Cholesterol (10 g.) with Al_2O_3 at 200°/1 mm. for 2 hr. followed by distillation at 260—270°/1 mm. gives 3.5 g. of $\Delta^{2,4}$ -cholestadiene (I), m.p. 61°, $[\alpha]_D^{25} +114^\circ$ in $CHCl_3$. (I) (3.6 g. in $EtOH$) exposed to sunlight for 14 days in presence of eosin gives 1.1 g. of a peroxide (II), $C_{27}H_{44}O_2$, m.p. 167°, $[\alpha]_D^{25} +140.5^\circ$ in $CHCl_3$. The absorption curve of (II) exhibits a weak max. at 238 m μ . (I) and (II) cause hyperkeratosis and loss of hair when applied to the skin of the mouse. W. McC.

Syntheses of polycyclic compounds related to sterols. VI. G. A. R. KON and E. S. NARRACOTT (J.C.S., 1938, 672—676; cf. A., 1933, 1153).—Reduction of 2- β -1'-naphthylethylcyclopentanone (I) gives the corresponding pentanol, b.p. 168—174°/0.4 mm. (3:5-dinitrobenzoate, m.p. 194—195°), yielding by cyclisation (P_2O_5) and dehydrogenation (Se) 1:2-cyclopentenophenanthrene (II). Methylation of (I) yields the 2-*Me* derivative, b.p. 182°/0.2 mm. (*semicarbazone*, m.p. 209°), reduced by H_2 and catalyst to 2-methyl-2- β -1'-naphthylethylcyclopentanol (III), m.p. 69—71°, b.p. 214—220°/1 mm. (3:5-dinitrobenzoate, m.p. 186°), and by Na in moist Et_2O to the corresponding H_2 -derivative, b.p. 194°/1 mm. (3:5-dinitrobenzoate, m.p. 170°), which is cyclised (P_2O_5) to a hydrocarbon, $C_{18}H_{22}$, b.p. 159—170°/0.2 mm., yielding (II) on dehydrogenation. (III) is cyclised (P_2O_5) to the hydrocarbon (A), b.p. 208—212°/3 mm., 160—165°/0.5 mm. [$s-C_6H_3(NO_2)_3$ derivative, m.p. 104°] (cf. Harper, *et al.*, A., 1934, 288), also obtained by cyclisation ($AlCl_3$) of 2-methyl-1- β -1'-naphthylethyl- Δ^1 -cyclopentene, b.p. 132—140°/0.2 mm. [$s-C_6H_3(NO_2)_3$ derivative, m.p. 85°], obtained from the corresponding cyclopentanol and I. (III) is dehydrated (CS_2) to the corresponding Δ^5 -cyclopentene, b.p. 168—172°/0.5 mm. [$s-C_6H_3(NO_2)_3$ derivative, m.p. 102.5—103°], which could not be cyclised. (III) therefore undergoes a retro-pinacolic change in cyclisation to (A).

2-Methyl-1- β -phenylethyl- Δ^1 -cyclopentene, b.p. 143—144°/22 mm., from the corresponding cyclopentanol and I (cf. Kon, A., 1933, 1153), is oxidised ($KMnO_4$) to a diketone (*disemicarbazone*, m.p. 191—192°) and



(A.)

cyclised (AlCl_3) to 1-methyl-1:2-cyclopentano-1:2:3:4-tetrahydronaphthalene (IV) (cf. Kon, *loc. cit.*). 2-Methyl-2- β -phenylethylcyclopentanone, b.p. 136—137°/1 mm. (semicarbazone, m.p. 191—192°), from 2- β -phenylethylcyclopentanone and MeI, is reduced ($\text{Na-Et}_2\text{O}$) to the corresponding cyclopentanol (V), b.p. 161°/3 mm., which is cyclodehydrated (P_2O_5) to (IV). Dehydration of (V) by Tschugaev's method yields the corresponding Δ^5 -cyclopentene, b.p. 142°/23 mm., oxidation (KMnO_4) of which gives an acid, m.p. 184° (semicarbazone, m.p. 183°), probably $\text{CH}_2\text{Bz}\cdot\text{CMe}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. 2-Methyl-2- β -phenylethyl- Δ^6 -cyclohexene, b.p. 152—153°/20 mm., from dehydration (Tschugaev) of the corresponding cyclohexanol (VI), could not be cyclised. 2-Methyl-1- β -phenylethyl- Δ^1 -cyclohexene, b.p. 153—154°/14 mm., from the corresponding cyclohexanol, b.p. 168—175°/17 mm., and I (xanthate reduction gives a product, b.p. 161—163°/23 mm.), gives on oxidation a diketone (disemicarbazone, m.p. 175°) and on cyclisation (AlCl_3) 12-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. 162—163°/18 mm., identical with the product, previously described as the 11-Me derivative, of cyclodehydration of (VI) (cf. Kon, *loc. cit.*). E. G. B.

Carcinogenic hydrocarbons. II. Ethylcholanthrene. W. F. BRUCE and S. J. KAHN (J. Amer. Chem. Soc., 1938, 60, 1017—1019; cf. A., 1937, II, 184).—Heating $p\text{-C}_6\text{H}_4\text{EtBr}$, $(\text{CH}_2\text{O})_3$, and $\text{ZnCl}_2\text{-AlCl}_3$ at 40—50° and treating the product with HCl gives a mixture, b.p. 128—131°/12 mm., of 1-bromo- α -chloromethyl-4-ethylbenzenes and 1-bromo- α -di-(chloromethyl)-4-ethylbenzene, m.p. 83°. The mixture with $\text{CHNa}(\text{CO}_2\text{Et})_2$ gives 78% of a mixture, b.p. 154—172°/0.8 mm., of $\text{Et}_2\text{x-bromo-y-ethylbenzylmalonates}$ (and a substance, b.p. 225—230°/0.8 mm.), converted successively into the corresponding acids, m.p. 165—166° (decomp.); β -x-bromo-y-ethylphenylpropionic acids, b.p. 156—160°/1 mm., and x-bromo-y-ethylhydrindones, b.p. 166—168°/14 mm., m.p. 77—78°, converted by Clemmensen reduction into 4-bromo-7-ethylhydrindene (I) (45% over-all yield), b.p. 145°/17 mm. This gives 4-cyano-7-ethylhydrindene, b.p. 152—156°/14 mm., and thence by $1\text{-C}_{10}\text{H}_7\text{-MgBr}$ yields the ketimine hydrochloride, decomp. 216—218°, hydrolysed to 4- α -naphthoyl-7-ethylhydrindene (II), b.p. 205—210°/0.5 mm., which is obtained in very poor yield from the Grignard reagent of (I) and $\alpha\text{-C}_{10}\text{H}_7\text{-COCl}$. At 405—410° (II) gives 20-ethylcholanthrene (III), m.p. 179.5—180° (corr.). The Grignard reagent of (I) with $\alpha\text{-C}_{10}\text{H}_7\text{-CHO}$ gives 38% of α -naphthyl-4-7-ethylhydrindenylcarbinol, b.p. 222—225°/1 mm., and 25% of 4-ethylhydrindene, b.p. 71—72°/2.5 mm.; the carbinol is converted by CrO_3 in $\text{AcOH-H}_2\text{SO}_4$ into di-(α -naphthyl-4-7-ethylhydrindenylcarbonyl) ether, b.p. 225—230°/1.5 mm., which gives (III) on pyrolysis. R. S. C.

Physiologically active phenylethylamines. II. Hydroxy- and methoxy- β -phenyl-n-propylamines. E. H. WOODRUFF and E. PIERSON (J. Amer. Chem. Soc., 1938, 60, 1075—1077; cf. A., 1938, II, 132).—The toxicity of $\text{CHMeAr}\cdot\text{CH}_2\cdot\text{NH}_2$ is < that of $\text{CH}_2\text{Ar}\cdot\text{CHMe}\cdot\text{NH}_2$. By standard reactions the appropriate acetophenones yield Et

β -m-anisylcrotonate, b.p. 171°/13 mm., β -o- (mixture of isomerides), m.p. 76°, β -m-, m.p. 100°, and β -p-anisylcrotonic acid, m.p. 154—155°, β -o-, b.p. 171°/11 mm., m.p. 47° (amide, m.p. 125—126°), β -m-, b.p. 190°/15 mm. (amide, m.p. 71°), and β -p-anisylbutyric acid, m.p. 65°, b.p. 188—190°/12 mm. (amide, m.p. 112°), β -phenyl- (hydrochloride, m.p. 146—147°; benzoate, m.p. 85—86°), β -o-, b.p. 121—123°/13 mm. (hydrochloride, m.p. 134—135°), β -m-, b.p. 130—132°/14 mm. (hydrochloride, m.p. 124°), and β -p-anisyl-n-propylamine, b.p. 130—131°/14 mm. (hydrochloride, m.p. 152—153°), β -o-, m.p. 168—169°, β -m-, m.p. 126—127°, and β -p-hydroxyphenyl-n-propylamine hydrochloride, m.p. 157—159°. The prep. of intermediates is modified. R. S. C.

Properties of β -phenylisopropylamine. J. HALD and I. GAD (Dansk Tidsskr. Farm., 1938, 12, 97—104).—Physical consts. of $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{NH}_2$ (I) and its salts have been redetermined. d-(I) and its sulphate have $[\alpha]_D^{20} + 35^\circ$ in EtOH, and $+22.5^\circ$ in H_2O , respectively. (I) may be determined by Kjeldahl determinations and identified by the benzoate, or (in small amount) by the red product, m.p. 121.5—123.5°, formed with $\text{K}_2\text{Pt}(\text{CNS})_6$.

M. H. M. A.

β -p-Hydroxyphenylisopropylmethylamine.—See B., 1938, 626.

Attempted resolution of phenylpentadeutero-phenylmethylamine. R. ADAMS and D. S. TARBELL (J. Amer. Chem. Soc., 1938, 60, 1260—1262).— C_6D_6 , m.p. 6.5° (92.5% pure), gives $(\text{BzCl-AlCl}_3\text{-CS}_2)$ 2:3:4:5:6-pentadeutero-benzophenone, m.p. 47—48°, the oxime, m.p. 142—143°, of which is reduced by Na-Hg to phenylpentadeutero-phenylmethylamine, $\text{C}_6\text{D}_5\cdot\text{CHPh}\cdot\text{NH}_2$, which was not resolved by way of the H d-tartrate, m.p. 175—180° (decomp.), $[\alpha]_D^{20} + 12.1^\circ$ in H_2O , or d-bromocamphorsulphonate, m.p. 237—239° (decomp.), $[\alpha]_D^{20} + 62.1^\circ$ in 95% EtOH. The resolution reported by Clemon *et al.* (A., 1936, 977) was due to use of impure C_6D_6 .

R. S. C.

Possible asymmetry of a monosubstituted cyclononane. C. S. MARVEL and D. B. GLASS (J. Amer. Chem. Soc., 1938, 60, 1051—1053).—cyclo-Octanone, m.p. 168—169°, and cyclononanone-semicarbazone, m.p. 178—179°, with $\text{H}_2\text{-PtO}_2$ in HCl-50% aq. MeOH give cyclooctyl-, m.p. 183° (d-camphor-10-sulphonate, m.p. 169—170°; $[\alpha]_D^{25} 26.4 \pm 1^\circ$ in CHCl_3), and cyclononyl-semicarbazide (I), m.p. 156°. (I) could not be resolved by way of the d-camphor-10-, m.p. about 97—112°, $[\alpha]_D^{25} + 19.9 \pm 0.5^\circ$ in MeOH, or d- α -bromocamphor- π -sulphonate, m.p. 106—111°, $[\alpha]_D^{25} 58.3 \pm 0.5^\circ$ in MeOH, in contradiction to demands of the Stuart model (A., 1935, 432), which, moreover, does not allow easy interchange of the boat and chair forms of C_9H_{16} . Stuart models are thus too inflexible. R. S. C.

Thermal studies of binary and ternary systems. I. Binary system acetanilide-phenacetin.—See A., 1938, I, 359.

Condensation of arylamines with diacetyl-tartaric anhydride. A. WRÓBEL (Rocz. Chem., 1938, 18, 16—17).—Małachowski's (A., 1937, II,

176) and Kuczyński's (*ibid.*, 375) objections to Wróbel's results (A., 1934, 309; 1937, II, 77) are admitted.

R. T.

Structure and pharmacological properties of substances containing the SO_2NHR group.

(A) Preparation of sulphonamides of aniline, α -naphthylamine, and *o*-, *m*-, and *p*-toluidines. (B) Preparation of certain azo-dyes containing the sulphonamide group. I. L. N. GOLDBREV and I. J. POSTOVSKI (J. Appl. Chem. Russ., 1938, 11, 316—327).—The following compounds have been prepared by the reactions: acetylarsamide + $\text{ClSO}_3\text{H} \rightarrow p$ -acetarsylaminesulphonyl chloride $\rightarrow (+\text{NH}_2\text{R}$ or $\text{NHR}'') p$ -acetamidarsylsulphonamide $\rightarrow (+\text{H}_2\text{O}) p$ -aminoarsylsulphonamide: *p*-acetamidobenzene-sulphon-piperidide, m.p. 156°, -benzylamide, m.p. 149°, and 2-pyridylamide, m.p. 196°; *p*-aminobenzene-sulphon-piperidide, m.p. 165° (hydrochloride, m.p. 181°), and -benzylamide, m.p. 107° (hydrochloride, m.p. 225°); α -naphthylamine-4-sulphon-piperidide, m.p. 141° (Ac derivative, m.p. 161°); *p*-toluidine-*o*-sulphonamide, m.p. 165° (Ac derivative, m.p. 239°; acetate, m.p. 234°); *m*-toluidine-6-sulphonamide, m.p. 168° (Ac derivative, m.p. 202°; acetate, m.p. 233°); *o*-toluidine-4-sulphonamide (Ac derivative, m.p. 228°; hydrochloride, m.p. 243°). The amines are diazotised, and coupled with $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ or *J*-acid, to yield the following azo-dyes: 2:4-diaminoazobenzene-4'-sulphon-benzylamide, m.p. 195°, and -(2-pyridylamide); 2:4-diamino-3'-methylazobenzene-4'-, m.p. 200°, and 2:4-diamino-6'-methylazobenzene-3'-sulphonamide, m.p. 199°; 1-(2':4'-diaminobenzeneazo)naphthalene-4-sulphonamide, m.p. 237°; Na salts of 6-amino-2-benzeneazo-3-sulpho- α -naphthol-4'-sulphonamide and -piperidide. Me-orange and excess of ClSO_3H yield 4-dimethylaminoazobenzene-4'-sulphonyl chloride, m.p. 150—155°, which with NH_3 gives 4-dimethylaminoazobenzene-4'-sulphonamide, m.p. 237—238°; 1-benzene-azo- β -naphthol-4'-sulphonyl chloride, m.p. 185°, and -sulphonamide, m.p. 277°, are prepared analogously from β -naphthol-orange.

R. T.

Action of hydroxyethylamine on nitro-derivatives of dimethylaniline with a mobile nitro-group, and on halogenated nitrobenzene derivatives with a mobile halogen atom. P. VAN ROMBURGH and C. W. ZAHN (Rec. trav. chim., 1938, 57, 437—444).—Anhyd. $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ (I) heated with 3:4:1- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NMe}_2$ (alone) and 3:4:6:1- $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{NMe}_2$ (in $\text{EtOH}-\text{COMe}_2$) yields respectively 4-nitro-, m.p. 156—158°, and 4:6-dinitro-3- β -hydroxyethylaminodimethylaniline, m.p. 204—205°. With 2:3:4:1- $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{NMe}_2$, 2:4-dinitro-1:3-di-(β -hydroxyethylamine)benzene, m.p. 140—141°, is produced with excess of (I) (alone) at 100°; 2:4-dinitro-3- β -hydroxyethylaminodimethylaniline, m.p. 98—101°, is also formed in EtOH . With 2:3:4:6-tetranitrophenylmethylnitroamine, (I) reacts violently and yields a substance, m.p. 147.5—148.5°; with picryl chloride, β -hydroxyethylpicramide, m.p. 109—110°, is formed, and with 1:2:4- $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2)_2$, 2:4-dinitro- β -hydroxyethylamine, m.p. 175—176°, is obtained.

J. D. R.

Free radicals from benzidine and its derivatives. J. WEISS (Chem. and Ind., 1938, 517—

518).—General considerations indicate that the primary blue product of the photosensitised oxidation of benzidine should be formed by a simple electron transfer to the excited dye mol. (D^*) thus: $D^* + \text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 = D^- + \text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2^+$, and should therefore be a positive benzidine ion. Study of the literature confirms this view and indicates that these positive ions are to be regarded as semiquinonoid radicals $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2^+ \rightleftharpoons \text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH} + \text{H}^+$. Their reduction by 1 H to the original compound is readily understood. The blue salts are salts of these positive ions with the corresponding anions. The further oxidation of the radical to $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}$ appears to be established by the isolation of the compound $(\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N})_2$ (Willstätter *et al.*, A., 1906, i, 996), by oxidation of the blue compound with PbO_2 .

H. W.

Manufacture of diarylarylenediamines.—See B., 1938, 626.

cis-Form of azobenzene and the velocity of the thermal *cis* \rightarrow *trans*-conversion of azobenzene and some derivatives. G. S. HARTLEY (J.C.S., 1938, 633—642; cf. A., 1937, 454).—The equilibrium mixtures obtained by exposure of dil. solutions of *cis*-(I), m.p. 71.4°, or *trans*-azobenzene to daylight contain 15—40% of (I), according to the solvent. The velocity of the thermal *cis* \rightarrow *trans*-conversion in the dark of azobenzene, its 4-OH-, 4-NH₂-, 4-NMe₂-, and 4-OMe-derivatives, and *p*-NMe₃⁺·C₆H₄·N[−]NPh salts in various solvents has been measured photo-metrically. Bases catalyse the conversion in H₂O of the OH-, and acids of the NH₂- (more sensitive) and NMe₂-derivatives, and (much less) of azobenzene itself.

A. LI.

Alkanolamines. IV. Reducing power of the amino-alcohols. C. B. KREMER and B. KRESS. **V. Reaction of *m*-dinitrobenzene with ethanolamines.** M. MELTSNER, I. KIRSHENBAUM, and A. STEMPER (J. Amer. Chem. Soc., 1938, 60, 1031—1032, 1236—1237).—IV. The amount of $(\text{NPh})_2 + \text{NH}_2\text{Ph}$ or $(m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{N})_2 + m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ formed from PhNO_2 or $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, respectively, is a max. when 2 C separate the OH and N of NH₂-alcohols used as reducing agents. Addition of NaOH increases the yield of azo-compound at the expense of the amine. Conditions materially affect the yields. $\text{NEt}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ has little reducing action and gives only $\text{NPh}\cdot\text{NO}\cdot\text{Ph}$. Imines are also formed, $(\text{CH}_2)_2\text{NH}$ and piperidine being identified. Amines used were $\text{NH}_2\cdot[\text{CH}_2]_x\cdot\text{OH}$ ($x = 2, 3$, and 5), $\text{NH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$, $\text{NH}([\text{CH}_2]_2\cdot\text{OH})_2$, $\text{N}([\text{CH}_2]_2\cdot\text{OH})_3$, $\text{NH}(\text{CH}_2\cdot\text{CHMe}\cdot\text{OH})_2$, and $\text{N}(\text{CH}_2\cdot\text{CHMe}\cdot\text{OH})_3$.

V. With boiling $\text{NH}([\text{CH}_2]_2\cdot\text{OH})_2$ $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ gives $(m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N})_2$, and, if 17% of H₂O is added, gives $(m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N})_2$ (I) and a little $m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\text{-}m$ (II) and (?) $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$. With $\text{N}([\text{CH}_2]_2\cdot\text{OH})_3$ (III) at 160—170° it gives $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{-}m$ and a mol. compound (IV), 2(II), (III), m.p. 109° [gives the Ac derivative of (I) when acetylated]; with an excess of boiling (III) it gives (I) and (IV). The formation of (IV) shows that addition precedes reduction. *m*-

$C_6H_4(NH_2)_2$ was not isolated, probably owing to its decomp. R. S. C.

Reaction of azo-dyes with nitrous acid. I, II. I. M. KOGAN and M. A. TSCHERKALIN (J. Appl. Chem. Russ., 1938, 11, 456—464, 465—470).—I. Me-orange reacts with excess of HNO_2 at 0—40°, yielding diazobenzene-4-sulphonic acid (I), $p-NMe_2 \cdot C_6H_4 \cdot NO_2$, and 3-nitro-4-dimethylaminoazobenzene-4'-sulphonic acid.

II. The sole product of reaction of HNO_2 with 4-aminoazobenzene-4'-sulphonic acid is the 4-diazo-derivative. With 4-benzeneazo- α -naphthylamine-4'-sulphonic acid the products are (I), 1-nitro-4-naphthalenediazonium chloride, and 1-diazo-4-benzeneazo-naphthylamine-4'-sulphonic acid. R. T.

Diazo-coupling of carcinogenic hydrocarbons. L. F. FIESER and W. P. CAMPBELL (J. Amer. Chem. Soc., 1938, 60, 1142—1145).— $p-NO_2 \cdot C_6H_4 \cdot N_2Cl$ couples rapidly (<5 min.) with 3:4-benzpyrene (I), 20-methylcholanthrene (II), cholanthrene, 8:9- and 4:10-ace-1:2-benzanthracene (III), 1:2-cyclopenteno- and 1:2-dimethyl-5:10-aceanthrene (IV), slowly (15—20 hr.) with anthracene, mesitylene, acenaphthene, acephenanthrene, 1-methyl-8:9-acephenanthrene, 9-methyl-1:2-benzanthracene, 1':9-methylene-1:2:5:6-dibenzanthracene, 15:16-benzdehydrocholanthrene, and not at all with 1:2-benzanthracene, 10-alkyl-, 5:10-dimethyl-, and 5-methyl-1:2-benzanthracene, 1:2:5:6-dibenzanthracene, pyrene, or chrysene. A rough, but far from rigid, correlation exists between ease of coupling and carcinogenicity. Except for (I), all the substances coupling readily are aceanthrene derivatives. The only p -nitrobenzeneazo-derivative isolable was that of (I), which has m.p. 245—246° (corr.). 2:4-(NO_2) $_2C_6H_3 \cdot N_2Cl$ couples with some of the compounds at comparable rates. (II) couples slowly with PhN_2Cl , $p-SO_3H \cdot C_6H_4 \cdot N_2Cl$, and 2:4- $SO_3H \cdot C_6H_3(NO_2)_2 \cdot N_2Cl$. 1:2 p.p.m. of (I) or 2:4 p.p.m. of the other reactive compounds can be detected by this reaction. (III), but not (IV), is carcinogenic when injected subcutaneously in lard into mice. R. S. C.

Phosphoric acid as catalyst in the ethylation of phenol. V. N. IPATIEV, H. PINES, and L. SCHMERLING (J. Amer. Chem. Soc., 1938, 60, 1161—1162).—At 225°/95 atm. C_2H_4 and $PhOH$ in presence of H_3PO_4 give ethylphenols, ethylphenetoles, and $PhOEt$. In cyclohexane more phenols and less ethers are formed. $PhOEt$ and C_3H_6 at 145° in presence of H_3PO_4 give only propylphenetoles, showing that ether formation is not necessarily an intermediate step in alkylation. $PhOEt$ is not rearranged under the conditions used. p -, new m.p. 96°, and o -Ethylphenoxyacetic acid, m.p. 136—137°, are described. R. S. C.

Action of nitrous acid on p -cresol and tyrosine. J. ST. L. PHILPOT and P. A. SMALL (Biochem. J., 1938, 32, 534—541).— p -Cresol reacts with HNO_2 in the presence of excess of $CuSO_4$ to yield a stable Cu di-3-nitroso- p -cresol, $C_{14}H_{12}O_4N_2Cu$; in the absence of Cu , 3-diazo- p -cresol is rapidly formed. Diazode-aminotyrosine is similarly formed from tyrosine and

is stable between 0° and 40°. Diazo- p -cresol couples with $\beta-C_{10}H_7 \cdot OH$ in alkaline solution yielding a compound, m.p. 109°. 3-Nitroso- p -cresol, m.p. 58.5°, forms a red Hg compound at p_H 3—4, sol. in $CHCl_3$, which differs from the red substance (insol. in $CHCl_3$) obtained in the Millon reaction, but can also be derived from it. P. G. M.

Syntheses in the phenanthrene series. IX. 6-Methoxy-1-methylphenanthrene. H. PLIMMER, W. F. SHORT, and (in part) P. HILL (J.C.S., 1938, 694—697).—2-Methylcyclohexanone and the Grignard compound of β - p -anisylethyl chloride, b.p. 129.5—131°/10 mm. (from the alcohol, $SOCl_2$, and C_5H_5N), yield 1- β - p -anisylethyl-2-methylcyclohexan-1-ol, b.p. 173—175°/5 mm., dehydrated ($KHSO_4$) to the cyclohexene, b.p. 156—156.5°/6 mm. Cyclisation ($AlCl_3$ in CS_2) followed by dehydrogenation (S) gives an oil affording a picrate, m.p. 114—116°, which when hydrolysed and demethylated yields a phenol, $C_{15}H_{12}O$, m.p. 104—108° (? 3-hydroxyphenanthrene). γ - p -Anisylbutyryl chloride with Et sodio- α -acetylglutarate in Et_2O , followed by hydrolysis (cold aq. KOH), thermal decomp., and successive treatment with hot 2N-NaOH and CH_2N_2 , gives the Me ester, m.p. 52°, of 8-keto- η -anisylcotic acid, m.p. 68° (poor yield). The Me ester with NaOEt in Et_2O yields 2- β - p -anisylethylcyclohexane-1:3-dione, m.p. 167—169°, cyclised by P_2O_5 to 1-keto-6-methoxy-1:2:3:4:9:10-hexahydrophenanthrene [2:4-dinitrophenylhydrazone, m.p. 230—232° (decomp.)] in very small yield. 1-Keto-7-methoxy-1:2:3:4-tetrahydronaphthalene (from p -anisylbutyric acid and P_2O_5 in C_6H_6 , or the acid chloride and $AlCl_3$ in $C_2H_2Cl_4$) with $CH_2Br \cdot CO_2Et$ and Zn in C_6H_6 , followed by reduction with Na + EtOH, yields β -(methoxy-tetrahydro-1-naphthyl)ethyl alcohol, b.p. 165°/0.4 mm. (3:5-dinitrobenzoate, m.p. 119.5—120°) (together with a little of the 1-naphthylacetic acid, m.p. 88—89°). The corresponding bromide, b.p. 155—160°/0.4 mm., with $CHK(CO_2Et)_2$ in $PhMe$ gives the substituted Et malonate, b.p. 220—230°/0.6 mm., hydrolysed and decarboxylated to a H_4 -acid which when heated with S affords γ -7-methoxy-1-naphthylbutyric acid, m.p. 105—106°. Cyclisation (P_2O_5) of this yields 1-keto-6-methoxy-1:2:3:4-tetrahydrophenanthrene [2:4-dinitrophenylhydrazone, m.p. 261—262° (sinters 256°)], which with $MgMeI$ followed by hydrolysis and dehydrogenation (S) gives 6-methoxy-, m.p. 87—87.5° (picrate, m.p. 140—141.5°), hydrolysed by $HBr \cdot AcOH$ to 6-hydroxy-1-methylphenanthrene, m.p. 161°, identical with the dehydrogenation product of podocarpic acid. A. LI.

Titration of quinol with dichromate. G. A. PEVTVZOV (Zavod. Lab., 1938, 7, 110).—Accurate titration of quinol with $K_2Cr_2O_7$ is not possible, owing to oxidation of the indicator ($NHPh_2$); more satisfactory results are given by running the quinol into $K_2Cr_2O_7$ and adding the indicator towards the end of the titration. R. T.

Introduction of the triphenylmethyl group. V. Mobility of the bromine atom in triphenylmethylisochavibetol [dibromide] and in its derivatives. II. E. FUNAKUBO and T. MATSUI (Ber., 1938, 71, [B], 942—947; cf. A., 1937, II, 454).—The

activation of a Br atom, probably in the α -position in the side-chain, by CPh_3 in triphenylmethylisochavibetol dibromide is observed also in the corresponding alkyl ethers. Triphenylmethylisochavibetol [6-methoxy-2-triphenylmethyl-3- Δ^a -propenylphenol] is converted by KOH-EtOH and the requisite alkyl iodide into the corresponding *Et*, m.p. 166–167°, *Pr^a*, m.p. 158–160°, *Pr^{\beta}*, m.p. 156–158°, *Bu^a*, m.p. 142–145°, *Bu^{\beta}*, m.p. 136–137°, and *isoamyl*, m.p. 115–116°, *ethers*. These are converted by Br in Et_2O at room temp. into the corresponding *dibromides*, m.p. 141.5–142°, 133–135°, 141–143°, 127–128°, 122–123°, and 102–103°, respectively, all with slow evolution of gas. The latter compounds are transformed by boiling MeOH into the following β -bromo- α -methoxytriphenylmethyldihydroisochavibetol alkyl ethers: *Et* (I), m.p. 161–162°, *Pr^a*, m.p. 154–155°, *Pr^{\beta}*, m.p. 159–160°, *Bu^a*, m.p. 146–148°, *Bu^{\beta}*, m.p. 153–154°, *isoamyl*, m.p. 147–148° (all with slow evolution of gas), and by boiling EtOH into the β -bromo- α -ethoxytriphenylmethyldihydroisochavibetol alkyl ethers: *Et*, m.p. 152°, *Pr^a*, m.p. 144–145°, *Pr^{\beta}*, m.p. 150–151°, *Bu^a*, m.p. 136–138°, *Bu^{\beta}*, m.p. 144–145°, *isoamyl*, m.p. 138.6–139° (all with slow evolution of gas). Ethylation of β -bromo- α -methoxytriphenylmethyldihydroisochavibetol affords (I). *isoChavibetol Et ether* is transformed by Br in Et_2O at -5° to $\sim 0^\circ$ into the *dibromide*, m.p. 120–120.5°, unchanged by short boiling with MeOH and partly resinified by longer boiling with EtOH . H. W.

Introduction of the triphenylmethyl group.
VI. Derivatives of triphenylmethylisoeugenol. E. FUNAKUBO and S. HASEGAWA (Ber., 1938, 71, [B], 947–949).—The constitution of triphenylmethylisoeugenol (A., 1936, 1388) is further confirmed by its conversion by the requisite alkyl iodide and KOH in boiling aq. MeOH into the *Me*, m.p. 137–138°, *Et*, m.p. 134–135.5° *Pr^a*, m.p. 126–127.5°, *Pr^{\beta}*, m.p. 153–155°, *Bu^a*, m.p. 103–104°, *Bu^{\beta}*, m.p. 129.5–131°, and *isoamyl*, m.p. 97.5–98.5°, *ethers* and by BzCl in anhyd $\text{C}_5\text{H}_5\text{N}$ at room temp. into the *benzoate*, m.p. 216.5–217.5°. H. W.

Reaction between 2:4-dinitrochlorobenzene and polyhydric phenols. E. FUNAKUBO, M. IMOTO, and E. IMOTO (Ber., 1938, 71, [B], 950–957).—Treatment of the monoethers of *o*-dihydric phenols with 1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ and NaOH in boiling $\text{EtOH-H}_2\text{O}$ gives the 2:4-dinitrophenyl ethers of *isoChavibetol*, m.p. 119°, *triphenylmethylisochavibetol*, m.p. 186–186.5°, *allylisochavibetol*, m.p. 140.5–141.5°, *isoeugenol*, m.p. 129.5°, *triphenylmethylisoeugenol*, m.p. 173–177.5°, and *ethylvanillin*, m.p. (indef.), 110–118°. With 1:2- $\text{C}_{10}\text{H}_6(\text{OH})_2$, 1:2-dihydroxyanthraquinone, and compounds 4:2:1- $\text{C}_6\text{H}_3\text{R}(\text{OH})_2$ in which $\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{CO}_2\text{H}, \text{CO}_2\text{Et}, \text{Ac},$ or COEt , the product is 2:4-dinitrophenetole (I) (formation discussed). 1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ is not appreciably affected by hot H_2O or abs. EtOH . Aq. NaOH partly converts it into 2:4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{OH}$ (II) whilst $\text{H}_2\text{O-NaOH-EtOH}$ affords (I) and (II). The latter is largely unchanged by hot H_2O , $\text{EtOH-H}_2\text{O}$, $\text{N-}, 0.1\text{N-},$ or 0.01N-NaOH , or EtOH-21\% HCl . H. W.

Constitution of croweacin. A. R. PENFOLD, G. R. RAMAGE, and J. L. SIMONSEN (J.C.S., 1938, 756–758; cf. J. Proc. Roy. Soc. New South Wales, 1923, 56, 227).—Croweacin acid is 2-methoxy-3:4-methylenedioxybenzoic acid (I), m.p. 153° [Br gives 1:5:6-tribromo-2-methoxy-3:4-methylenedioxybenzene (II)], and croweacin is 2-methoxy-3:4-methylenedioxypropenylbenzene (III) (Br in AcOH yields the Br_2 -derivative *dibromide*, m.p. 108°). KMnO_4 in COMe_2 oxidises (III) to (I) and the *glycol*, m.p. 97°, converted by $\text{Pb}(\text{OAc})_4\text{-AcOH}$ into (V) (below). *Daphnetin* and $\text{CH}_3\text{SO}_4\text{-KOH}$ in COMe_2 yield the *methylene ether*, m.p. 188°, which with $\text{Me}_2\text{SO}_4\text{-NaOH}$ gives α -2-methoxy-3:4-methylenedioxypropenylbenzoic acid (IV), m.p. 131°, oxidised (O_3 in aq. Na_2CO_3) to 2-methoxy-3:4-methylenedioxybenzaldehyde (V), m.p. 104° (*semicarbazone*, m.p. 238°; 2:4-dinitrophenylhydrazone, m.p. 254°), converted by KMnO_4 in aq. COMe_2 at 40° into (I). (IV) is probably the *cis*-form and a β -isomeride, m.p. 212–213°, is obtained from $\text{CH}_2(\text{CO}_2\text{H})_2$ and (V) in $\text{C}_5\text{H}_5\text{N}$ -piperidine. Anhyd. 2:3:4- $(\text{OH})_3\text{C}_6\text{H}_2\text{CO}_2\text{Me}$, m.p. 153° ($+2\text{H}_2\text{O}$, m.p. 148°), and CH_2N_2 in Et_2O yield an ester which with KOH-EtOH gives 2:3:4- $(\text{OH})(\text{OMe})\text{C}_6\text{H}_2\text{CO}_2\text{H}$ and 2:3:4- $(\text{OH})_2(\text{OMe})\text{C}_6\text{H}_2\text{CO}_2\text{H}$, new m.p. 222°. 2:3:4- $(\text{OH})_2(\text{OMe})\text{C}_6\text{H}_2\text{CO}_2\text{Me}$, m.p. 101°, and $\text{CH}_3\text{SO}_4\text{-KOH}$ form *Me 4-methoxy-2:3-methylenedioxybenzoate*, m.p. 122–123°, hydrolysed by 8% NaOH to the *acid*, m.p. 256°. The latter or the 5-*OMe*-isomeride and Br afford (II). A. T. P.

Naphthol series. A. LEMAN (Ann. Chim., 1938, [xi], 9, 357–446; cf. A., 1935, 856; 1936, 602).—The formation of 1:7- $\text{C}_{10}\text{H}_6(\text{OH})_2$ (I) from 2:8- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ by alkali fusion in an autoclave or open vessel proceeds better with KOH or with $\text{KOH} + \text{NaOH}$ at 230–260° than with NaOH . Hydrolysis of 1:7:3- $\text{C}_{10}\text{H}_5(\text{OH})_2\text{SO}_3\text{H}$ to (I) proceeds best with 1.5N- HCl at 220–225°. The following derivatives of (I) (m.p. 181°; lit. 175–178°) are described: *di-p-nitrobenzoate*, m.p. 182–183°, *dicinnamate*, m.p. 125°, *diallophanate*, m.p. 243°. The rates of acetylation of α - and β - $\text{C}_{10}\text{H}_7\text{OH}$ with $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ or $\text{Ac}_2\text{O-AcOH-H}_2\text{SO}_4$ are equal, and $>$ those of 1:5-, 1:7-, or 2:7- $\text{C}_{10}\text{H}_6(\text{OH})_2$, the relative rates of which vary with concn. of Ac_2O . With $\text{Ac}_2\text{O-AcOH}$ the order is $\beta > \alpha\text{-C}_{10}\text{H}_7\text{OH}$, and 2:7- and 1:7- $>$ 1:5- $\text{C}_{10}\text{H}_6(\text{OH})_2$. With $\text{BzCl-C}_5\text{H}_5\text{N}$ the relative rates of reaction are $\beta > \alpha$ and 2:7 $>$ 1:7 $>$ 1:5. Nitrosation and coupling (with PhN_2Cl) of (I) probably take place predominantly in the 4-position; bromination and iodination lead largely to oxidation rather than substitution products. J. D. R.

Hydrogenated naphthalenes and their transformations. 5:6- and 5:7-Dihydroxy-1:2:3:4-tetrahydronaphthalene. G. SCHROETER [with K. ERZBERGER and L. PASSAVANT] (Ber., 1938, 71, [B], 1040–1056; cf. A., 1922, i, 122 *et seq.*).—Passage of Cl_2 into 1:2:3:4-tetrahydronaphthalene containing Fe wire and Fe filings at 0° gives unchanged material, a mixture of 5- (I) and 6- (II) -chloro-1:2:3:4-tetrahydronaphthalene (yield 70%), and more highly chlorinated products. (II) is unchanged by conc. H_2SO_4 at room temp. for 12 hr. whereas (I) is transformed into 5-chloro-1:2:3:4-tetrahydronaphthalene-

8-sulphonic acid (III), m.p. 80—81° [di- and monohydrate; Ba, Pb, Ag (+H₂O), and Na salts], the dihydrated Mg salt of which is converted by 70% H₂SO₄ and steam at 200° into (I), b.p. 118°/12 mm., identical with a specimen obtained from 5-amino-1:2:3:4-tetrahydronaphthalene (Sandmeyer). (II), b.p. 118·5°/12 mm., is identical with the substance obtained from 6-amino-1:2:3:4-tetrahydronaphthalene. Alternatively the mixture of (I) and (II) is completely sulphonated and the product is crystallised from C₆H₆, from which 6-chloro-1:2:3:4-tetrahydronaphthalene-7-sulphonic acid (+2H₂O) (IV), m.p. 130—131° [Ba, Pb, Mg (+7H₂O), and Na (+2H₂O) salts], separates or is neutralised with MgO and separated through the Mg salts. (IV) is inefficient for the catalytic hydrolysis of fats whilst (III) causes complete and rapid hydrolysis when used as the dihydrate but is less efficient as monohydrate. Since reaction occurs in the presence of steam it appears that the catalytic chain reaction commences with the union of (III) and a mol. of fat and that in this form (III) is unaffected by H₂O. Aq. NaOH in presence of Cu at 180° converts (IV) into Na 6-hydroxy-1:2:3:4-tetrahydronaphthalene-7-sulphonate (V) (yield 98%), transformed by boiling 30% HCl into 6-hydroxy-1:2:3:4-tetrahydronaphthalene, b.p. 154—155°/17 mm., m.p. 61·5—62·5°, in 90% yield. Similarly, (III) is converted into Na 5-hydroxy-1:2:3:4-tetrahydronaphthalene-8-sulphonate (+H₂O) [corresponding Ba (+2H₂O) salt], transformed by HNO₃ into the 6-nitro-5-hydroxy-1:2:3:4-tetrahydro-8-sulphonic acid and by boiling 30% HCl into 5-hydroxy-1:2:3:4-tetrahydronaphthalene, b.p. 147°/14 mm., m.p. 68—69°. Bromination of the Na salt of (V) gives Na 5-bromo-6-hydroxy-1:2:3:4-tetrahydronaphthalene-7-sulphonate, hydrolysed by 15% NaOH containing Cu wool at 140° to Na 5:6-dihydroxy-1:2:3:4-tetrahydronaphthalene-7-sulphonate (+H₂O) (VI). This with Me₂SO₄ and 35% NaOH affords Na 5:6-dimethoxy-1:2:3:4-tetrahydronaphthalene-7-sulphonate (+H₂O), hydrolysed (20% NaOH at 200—210°) to Na 6-hydroxy-5-methoxy-1:2:3:4-tetrahydronaphthalene-7-sulphonate (+H₂O). Boiling 30% HCl transforms (VI) into 5:6-dihydroxy-1:2:3:4-tetrahydronaphthalene, b.p. 158—160°/12 mm., m.p. 69—70° (diacetate, m.p. 96—97°; carbonate, m.p. 124—125°; Me₂ ether, b.p. 137—138°/12 mm.).

5-Amino-1:2:3:4-tetrahydronaphthalene-7-sulphonic acid is converted by NaNO₂ and 2N-H₂SO₄ into the corresponding diazo-compound, chars 210° (brown at 170°), transformed by boiling H₂O followed by NaOH into Na 5-hydroxy-1:2:3:4-tetrahydronaphthalene-7-sulphonate; this with NaOH at 280—320° affords α-C₁₀H₇·OH and Na₂SO₄. Similarly 6-amino-1:2:3:4-tetrahydronaphthalene-8-sulphonic acid gives Na 6-hydroxy-1:2:3:4-tetrahydronaphthalene-8-sulphonate, which affords β-C₁₀H₇·OH and 5:6:7:8-tetrahydro-β-naphthol when fused with NaOH. Na 1:2:3:4-tetrahydronaphthalene-7-sulphonate is converted by 25% oleum at 160° into Na₂ 1:2:3:4-tetrahydronaphthalene-5:7-disulphonate (corresponding disulphonyl chloride, m.p. 103—104°), which with NaOH affords α-C₁₀H₇·OH and 5:6:7:8-tetrahydro-α-naphthol. 5:7-Diamino-

1:2:3:4-tetrahydronaphthalene is transformed into the *H* oxalate, which when suspended in 2N-AcOH and cautiously treated with Ac₂O yields 5:7-diacetamido-1:2:3:4-tetrahydronaphthalene, m.p. 245—246°, and 5-amino-7-acetamido-1:2:3:4-tetrahydronaphthalene, m.p. 110—111°; this when diazotised and treated with Me₂SO₄ yields 7-acetamido-5-methoxy-1:2:3:4-tetrahydronaphthalene, m.p. 187—188°, hydrolysed to 7-amino-5-methoxy-1:2:3:4-tetrahydronaphthalene, m.p. 102—103°, the *H* sulphate of which yields the 7-hydroxy-5-methoxy-derivative, m.p. 85—86°. 5:7-Dihydroxy-1:2:3:4-tetrahydronaphthalene (VII), b.p. 203°/12 mm., m.p. 122°, is obtained by the hydrolysis of the 5:7-(NH₂)₂-derivative with 2N-HCl at 270—290°, whereby under milder conditions the 7-amino-5-hydroxy-compound, m.p. 177°, is obtained as intermediate product. (VII) yields a diacetate, b.p. 196°/15 mm., m.p. 39—40°, a dibenzoate, m.p. 116—118°, and a Me₂ ether, b.p. 154—156°/12 mm., m.p. 38·5—39·5°. Reduction of (VII) by Na-Hg or catalytically in BuOH or decahydronaphthalene gives inconclusive results; with H₂ at 165°/15 atm. and Ni-Cu-Co in absence of solvent there result tetrahydronaphthalene, (?) β-ketodecahydronaphthalene, β-decahydronaphthol, and, probably, 1:3-dihydroxydecahydronaphthalene (isolated as the bisphenylcarbamate, m.p. 208—209°). H. W.

Anionotropic changes of (+)- and (–)-α-phenylallyl alcohols. D. DUVEEN (Compt. rend., 1938, 206, 1185—1186).—Fractional crystallisation of the quinidine salt of the *H* phthalate of *dl*-α-phenylallyl alcohol affords the *H* phthalates of (+)- and (–)-α-phenylallyl alcohol. Catalytic reduction of the (–)-alcohol (obtained by hydrolysis of the *H* phthalate) affords CHPhEt·OH identical with the alcohol obtained by resolution of *dl*-CHPhEt·OH. The active *H* phthalates are much more stable than their γ-Me derivatives (Kenyon *et al.*, A., 1937, II, 146) and analogous compounds described by Burton (A., 1928, 880; 1929, 554). J. L. D.

Magnesium pentamethylphenyl bromide. J. SAVARD and R. HÖSÖGÜR (Rev. Fac. Sci. Istanbul, 1938, 3, 164—173).—C₆Me₅Br (I) does not react with Mg in Et₂O unless the reaction is initiated by, e.g., EtBr or allyl bromide (II). Decomp. of the mixed Grignard reagent from (I) and EtBr or (II) yields pentamethyl ethyl- (III), m.p. 125°, or -allylbenzene, m.p. 135°, respectively. The Grignard reagent from (I) and EtBr with CO₂ yields (III), C₆Me₅CO₂H, and EtCO₂H; with COMe₂, pentamethylisopropenylbenzene, sublimes 121°, and pentamethylphenyldimethylcarbinol, m.p. 134° (decomp.), are formed; with AcCl, (III), pentamethylphenylmethylethylcarbinol, m.p. 52°, and pentamethylacetophenone (IV), m.p. 151°, are obtained; with BzCl, (V) and pentamethylbenzophenone, m.p. 125° (semicarbazone, m.p. 170°), and with PhCHO, (III) and pentamethylbenzhydrol, m.p. 107·5°, are formed. The mixed Grignard reagent from (I) and MeI with EtOAc yields C₆Me₅ and (IV); with HCO₂Et or CH(OEt)₃, C₆Me₅ and pentamethylbenzaldehyde, m.p. 130·5°, are formed. J. D. R.

Hydrobenzoin and semihydrobenzoin changes with replacement of one or two aryl by other

radicals. M. TIFFENEAU (Helv. Chim. Acta, 1938, 21, 404—431).—A lecture. R. S. C.

Isomerism of the 4 : 4'-dinitrostilbene oxides. S. BODFORSS (Annalen, 1938, 534, 243—247).—Some of the reactions used by Barrow (Diss., Strassburg, 1909) are unsuited to the elucidation of the structure of the 4 : 4'-dinitrostilbene oxides, m.p. 201° (*trans*) (I) and 157—159° (*cis*) (II), obtained from $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, and alkali (cf. Bergmann and Hervey, A., 1929, 695). Thus (II) is converted into (I) by alkali whilst (I) and (II) with conc. H_2SO_4 in AcOH yield the same 4 : 4'-dinitrohydrobenzoin and with KI in AcOH afford the same *iodohydrin*, m.p. 180° (decomp.). The observations are in harmony with the conception that the compounds are *cis-trans*-isomeric oxides. The production of 4 : 4'-dinitrobenzophenone from (II) and HNO_3 [whereas (I) gives 4 : 4'-dinitrobenzyl] indicates that the intermediate formation of $(p\text{-NO}_2\cdot\text{C}_6\text{H}_4)_2\text{CH}\cdot\text{CHO}$ occurs more rapidly than the hydration, whereby it must be assumed that the primary effect of HNO_3 differs from that of H_2SO_4 . H. W.

Pyrenium [derivatives]. XXXI. Oxidation of carbenium salts by hydrogen peroxide. W. DILTHEY, F. QUINT, and H. DIERICH (J. pr. Chem., 1938, [ii], 151, 25—34; cf. A., 1938, II, 152).—The H_2O_2 -AcOH fission of carbenium, e.g., 9-arylxanthene, salts is applicable to $\text{CAr}_3\cdot\text{OH}$, yielding COAr_2 and ArOH . Thus, $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{ClO}_4$ gives COPh_2 and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ (I); $(p\text{-OMe}\cdot\text{C}_6\text{H}_4)_2\text{CPh}\cdot\text{ClO}_4$ gives $p\text{-COPh}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ and (I); $(p\text{-OMe}\cdot\text{C}_6\text{H}_4)_3\text{C}\cdot\text{ClO}_4$ gives $\text{CO}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ and (I); $(p\text{-OPh}\cdot\text{C}_6\text{H}_4)_2\text{CPh}\cdot\text{ClO}_4$ gives $p\text{-COPh}\cdot\text{C}_6\text{H}_4\cdot\text{OPh}$ and $p\text{-OPh}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ (II); $(p\text{-OPh}\cdot\text{C}_6\text{H}_4)_3\text{C}\cdot\text{ClO}_4$ gives $\text{CO}(\text{C}_6\text{H}_4\cdot\text{OPh})_2$ and (II). In 88% H_2SO_4 $(p\text{-NO}_2\cdot\text{C}_6\text{H}_4)_3\text{C}\cdot\text{OH}$ at 5—10° gives $\text{CO}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ (III) and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ (IV); in AcOH- HClO_4 there is no reaction; in 95% H_2SO_4 only (IV) and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (V) are obtained, as (III) is itself converted into these products in this medium. (III) gives a colour (salt-formation) in 95% H_2SO_4 , but in 88% H_2SO_4 , in which it is stable to H_2O_2 , it is colourless. In 95% H_2SO_4 $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OPh}$ gives (V) and PhOH . $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\text{Cl}$ in AcOH- CClO_4 gives $p\text{-COPh}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ and PhOH . $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_3$ in KOH-MeOH gives a blue solution (salt-formation), rendered colourless by H_2O_2 , which gives a 90% yield of $(p\text{-NO}_2\cdot\text{C}_6\text{H}_4)_3\text{C}\cdot\text{OH}$. The influence of substituents on the ease of fission of the Ar-C linking is that expected. $\text{CO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ and $\text{H}_2\text{O}_2\text{-HClO}_4$ give $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. R. S. C.

Deacylation of acyltriphenylmethylglycerols and their uses. I. P. E. VERKADE and J. VAN DER LEE (Rec. trav. chim., 1938, 57, 417—422).— α -Triphenylmethylglyceryl γ -stearate and $\beta\gamma$ -distearate, and $\alpha\gamma$ -di(triphenylmethyl)glyceryl β -stearate with NaOH-EtOH lose only the stearyl radical. $\alpha\gamma$ -Distearin and CPh_3Cl in quinoline yield β -triphenylmethylglyceryl $\alpha\gamma$ -distearate, two forms, m.p. about 50—51° and 64—64.5°, which with NaOH-EtOH yields β -triphenylmethylglycerol, m.p. 143—144°. Similar hydrolysis of $\alpha\beta$ -di(triphenylmethyl)glyceryl

γ -stearate yields $\alpha\beta$ -di(triphenylmethyl)glycerol, two forms, m.p. 142—143° and 145.5—146.5°. J. D. R.

Sterols and sexual hormones. XLII. Stereochemistry of epimeric sterol alcohols with a hydroxyl in position 3 or 17. L. RUZICKA, M. FURTER, and M. W. GOLDBERG (Helv. Chim. Acta, 1938, 21, 498—514).—In 14 examples sterol esters having O-acyl at C_{10} or C_{17} , are more rapidly hydrolysed when this is *trans* (Ruzicka's nomenclature) than when it is *cis*, thus confirming the nomenclature. Models show this to be due to steric hindrance if cholesterol is the *trans-trans-anti-trans-anti-trans*- and coprostanol the *cis-cis-anti-trans-anti-trans*-compound; alternative ring alignments give too thick a mol. Digitonide formation is due to the OH projecting more horizontally from a fiat mol. Other reactions may also have a steric explanation. For steric reasons ring B has the chair form and ring C probably the boat form; for ring A the two forms are interconvertible. R. S. C.

Sterols. XXXI. Oxidation of sitosterol by selenium oxide. R. E. MARKER, O. KAMM, and E. L. WITTE. XXXII. Oxidation of stigmasterol by selenium oxide. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1938, 60, 1071—1073, 1073—1075).—XXXI. Sitosteryl acetate and SeO_2 in C_6H_6 -98% AcOH give 4- (I), m.p. 184°, and 6-hydroxysitosterol, m.p. 250°, separated as diacetates, m.p. 167° (II) and 107°, respectively. (I) is also isolated directly as 3-acetate, m.p. 192°. Hydrogenation (PtO_2 , AcOH) of (II) gives 4-hydroxysitostanol diacetate (III), m.p. 153°, and thence 4-hydroxysitostanol (=4-hydroxystigmasteranol), m.p. 203°, which with CrO_3 gives an acid, $\text{C}_{29}\text{H}_{50}\text{O}_4$, m.p. 200—205° (Me_2 ester, m.p. 123—124°). Heating (II) in HCl-EtOH causes dehydration, yielding sitostenone. With CrO_3 4-hydroxycholestanol gives Diels' saturated acid, obtained also by $\text{Pb}(\text{OAc})_4\text{-H}_2\text{O}_2$.

XXXII. Stigmasteryl acetate and SeO_2 in C_6H_6 -98% AcOH yield 4-hydroxystigmasteryl acetate, m.p. 193—195° [isolated as such or by way of the diacetate (IV), m.p. 200—201°; yields 4-hydroxystigmasterol (V), m.p. 188°], and 6-hydroxystigmasterol, m.p. 237° (isolated from the diacetate mother-liquors). Hydrogenation of (IV) gives (III). With HCl-EtOH (V) is dehydrated to stigmastene. The above results afford further evidence that stigmasterol differs from sitosterol only in the presence of a double linking in the side-chain. R. S. C.

Sex hormones and related substances. XI. Position of the double linking in cinchol, the sterol of cinchona bark. W. DIRSCHERL and J. KRAUS (Z. physiol. Chem., 1938, 253, 64—70).—Cinchol (I) in C_6H_6 with Br in AcOH gives the dibromide (not isolated), oxidised by CrO_3 in AcOH and then debrominated by boiling EtOH-NaI; the final product yields the semicarbazone (II), m.p. 235—240° (decomp.), of cinchone (III), m.p. 90—92°, $[\alpha]_D^{25} +78.7^\circ$ in CHCl_3 . The absorption curves of (III) and (II) are almost identical with those of cholestenone and its semicarbazone, respectively, indicating that (III) is an $\alpha\beta$ -unsaturated ketone. (III) in EtOH treated successively with Pd- H_2 and $\text{PtO}_2\text{-H}_2$ gives epidihydrocinchol (IV), m.p. 141—

142° (corr.), $[\alpha]_D^{25} + 30^\circ$ in CHCl_3 (3:5-dinitrobenzoate, m.p. 199—200°), in which H at $\text{C}_{(5)}$ is *cis* to Me at $\text{C}_{(10)}$. The 3:5-dinitrobenzoate of the epidihydrocincholinol, m.p. 201° (A., 1936, 77), has m.p. 185—186° (sinters at 183°). (IV) forms an additive compound with dihydrocincholinol, m.p. 145—146°. The double linking is at $\text{C}_{(4)}$ — $\text{C}_{(5)}$ in (III) but probably at $\text{C}_{(5)}$ — $\text{C}_{(6)}$ in (I). W. McC.

Sterol group. XXXVI. Oxidation of *i*-cholesterol and its derivatives. I. M. HEILBRON, J. HODGES and F. S. SPRING (J.C.S., 1938, 759—760; cf. Wallis *et al.*, A., 1937, II, 99, 416).—Oxidation of *i*-cholesterol (I), its acetate (II), and Me ether (III) (more slowly) with CrO_3 at room temp. yields "heterocholestenone" (IV), m.p. 97°, $[\alpha]_D^{25} + 40.9^\circ$ in CHCl_3 (oxime, m.p. 123°), identical with that of Windaus and Dalmer (A., 1919, i, 203), and converted by HCl — AcOH at room temp. into α -3-chloro-6-ketocholestane. The ketone, m.p. 110—111°, obtained indirectly from (I) by Ford *et al.* (A., 1938, II, 137) is different from (IV) or is not homogeneous. (IV) and $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH give an alcohol [acetate (V), m.p. 60°, $[\alpha]_D^{25} + 82.4^\circ$ in CHCl_3 , possibly an epimeride of (II)], converted [as is (V)] by HCl — AcOH into cholesteryl chloride. (III) and CrO_3 in 80% AcOH at 97° yield solely 7-ketocholesteryl acetate. The structure assigned to (I) by Wallis *et al.* (*loc. cit.*) is confirmed. A. T. P.

Carotenoids from purple bacteria. IV. P. KARRER, U. SOLMSEN, and H. KOENIG (Helv. Chim. Acta, 1938, 21, 454—455; cf. A., 1936, 1561).—Rhodopin, $\text{C}_{40}\text{H}_{58}\text{O}_2$, has m.p. 171° (previous sintering), is epiphasic, and contains 1 OH, which is probably *tert.*, since it resists acetylation. Rhodovibrin, $\text{C}_{40}\text{H}_{56}\text{O}_2$, contains no OMe, but probably does not contain 2 OH, since it is epiphasic. The absorption spectrum of flavorhodin, m.p. 111—113°, is detailed. KMnO_4 -oxidation of rhodoviolascin gives six products, separable by adsorption on $\text{Ca}(\text{OH})_2$. R. S. C.

Steroids and related compounds. II. Dehydration of cholestanetriol. V. A. PETROW, O. ROSENHEIM, and W. W. STARLING (J.C.S., 1938, 677—681).—Cholestane-3:5:6-triol diacetate (*ibid.*, 1908, 93, 1681) with SOCl_2 in $\text{C}_5\text{H}_5\text{N}$ yields the diacetate of Δ^4 -cholestene-3:6-diol (I); the triol 3-benzoate 6-acetate similarly gives the benzoate acetate of (I). (I) is identical with the diol, m.p. 258°, obtained by oxidising (SeO_2) cholesteryl acetate (A., 1937, II, 191); the mechanism of this oxidation is discussed. Oxidation (CrO_3) of (I) yields the 3:6-dione, whilst reduction (PtO_2) followed by oxidation gives cholestane-3:6-dione. The constitution (I) has previously been assigned to compounds obtained from cholestanetriol and Ac_2O — H_2SO_4 (Westphalen, A., 1915, i, 884) and from 5-chlorocholestane-3:6-diol dibenzoate by pyrolysis (Lettré and Müller, A., 1937, II, 455). Westphalen's diol and its esters are strongly dextrorotatory, are resistant to catalytic hydrogenation, and give green colours with Br in AcOH . This diol with CrO_3 at room temp. gives a diketone, m.p. 105—106°, $[\alpha]_D^{25} - 45.7^\circ$ in CHCl_3 (bis-2:4-dinitrophenylhydrazones, m.p. 217—218°; mono-*o*-tolylsemicarbazone, m.p. 234—235°), and

it is suggested that the diol is 5-methyl- $\Delta^{8:9}$ -norcholestene-3:6-diol. Lettré's "diol" is identical with 6-ketocholestanol (II), new m.p. 142—143° (*p*-nitrophenylhydrazones, m.p. 196—197°; *o*-tolylsemicarbazone, m.p. 223—224°). The enol dibenzoate prepared (BzCl — Bz_2O) from 3-ketocholestanol is hydrolysed (EtOH — KOH) to (II). A. Li.

Sterols. XXIX. Urane derivatives. XXX. Structure of pregnanetriol-B. R. E. MARKER, O. KAMM, T. S. OAKWOOD, E. L. WITTLE, and E. J. LAWSON (J. Amer. Chem. Soc., 1938, 60, 1061—1066, 1067—1071).—XXIX. Pregnanetriol-A (A., 1938, II, 97) is shown to be urane-3:11:20-triol (I), urane being the hydrocarbon which differs from pregnane in the configuration at $\text{C}_{(9)}$. In the pregnane series a OH at $\text{C}_{(11)}$ is sterically hindered if *cis* to the two angular Me, but in urane if *trans*. Thus, Reichstein's substance, *M*, sarmentogenin, and (I) have a *cis*-OH at $\text{C}_{(11)}$, but digoxigenin and dihydrodeoxysarmentogenin have a *trans*-OH. With digitonin in EtOH (I) gives no ppt. and only a very slight one after treating with Na in xylene; it thus belongs to the coprostane series with regard to $\text{C}_{(5)}$. With CrO_3 in 90% AcOH it gives uranetrione (II), m.p. 245°, which gives only a bis-2:4-dinitrophenylhydrazones, m.p. 236° (decomp.), and disemicarbazone, m.p. >325°, proving presence of a CO [and thus of a OH in (I)] at $\text{C}_{(11)}$. This ketone is unchanged by HCl — AcOH . It is also isolated by oxidation of an appropriate fraction of human pregnancy urine, indicating the presence of (I) therein. With Br— AcOH it gives a Br-derivative, m.p. 204° (decomp.), converted by hot $\text{C}_2\text{H}_5\text{N}$ in good yield into urenetrione, anhyd., m.p. 196°, and + H_2O , m.p. 219°, which confirms the coprostane structure of $\text{C}_{(5)}$. With H_2 — PtO_2 in AcOH at 70°/3 atm. (II) absorbs 2H_2 readily, the CO at position 11 being only slowly attacked; the product, by the steps \rightarrow diolone acetates \rightarrow diol acetates \rightarrow diols \rightarrow diones, yields urane-3:20-dione (III), m.p. 182°, and pregnane-3:20-dione; it is uncertain at which stage inversion to the pregnane series occurs. Clemmensen reduction of (II) gives urane, m.p. 128°, and a small amount of (?) impure pregnane. *alloPregnane*, m.p. 84°, is similarly obtained from *allopregnanedione*. (III) is obtained by oxidising the mother-liquors from (I) and its *B*-isomeride, and furnishes urane when reduced.

XXX. Pregnanetriol-B (*loc. cit.*) is shown to be 3(α):4(β):20(α)-trihydroxypregnane (IV) (*tribenzoate*, m.p. 218°). Partial hydrolysis of its triacetate and subsequent oxidation gives a diolone diacetate (V), $\text{C}_{25}\text{H}_{38}\text{O}_5$, two forms, m.p. 188° and 170° (*semicarbazone*, m.p. >315°), which does not give Zimmermann's test for a $\text{C}_{(3)}$ -ketone and with $\text{Al}(\text{OPr}^i)_3$ gives a product which yields no digitonide. Clemmensen reduction of (V) gives *allopregnane*, which is explicable if the CO is at $\text{C}_{(20)}$. With PCl_5 (IV) gives an oil, converted by Na— EtOH into an unsaturated product, hydrogenation of which gives pregnane. The formation of pregnane and *allopregnane* in these reactions indicates presence of a OH at $\text{C}_{(4)}$ and this is confirmed by oxidation of (IV) by CrO_3 in 95% AcOH at 20° to a monobasic diketone-acid, forms, m.p. 94—98° and an oil [*Me*

ester, an oil; *semicarbazone*, m.p. 190° (decomp.); *dioxime*, m.p. 181—183°; lactonises; equiv. wt. about 350], which is obtained also by successive hydrogenation, hydrolysis, and oxidation of pregane-4:20-diol-3-one diacetate. Under other conditions (IV) is oxidised to *allopregnanedione*. HIO_4 and $\text{Pb}(\text{OAc})_4\text{-H}_2\text{O}_2$ are without effect on (IV); Na in xylene converts it into a substance, which gives a digitonide. R. S. C.

Constituents of the adrenal cortex. [XVII.] Substances *J*, *K*, *N*, and *O*. (FRLN.) M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 546—564; cf. A., 1938, II, 192).—Acetylation of the crude cryst. material from the "phenol- and ketone-free ether residue" from adrenal cortex in $\text{C}_5\text{H}_5\text{N}$ at room temp. and adsorption of the acetates on Al_2O_3 gives substance *J* (A., 1936, 1383), m.p. variable, $[\alpha]_D^{25} -7.9 \pm 1^\circ$ in abs. EtOH (*diacetate*, m.p. 161—162°, $[\alpha]_D^{25} +24.6 \pm 1^\circ$ in COMe_2), substance *K*, $\text{C}_{21}\text{H}_{36}\text{O}_4$, opaque at 140°, m.p. 198—200°, $[\alpha]_D^{25} -1 \pm 2^\circ$ in abs. EtOH (*triacetate*, m.p. 177—178°, $[\alpha]_D^{25} +53.2 \pm 1^\circ$ in COMe_2 ; *digitonide*), substance *O*, $\text{C}_{21}\text{H}_{36}\text{O}_3$, opaque at about 130°, m.p. 222—223°, $[\alpha]_D^{25} -12.55 \pm 2^\circ$ in abs. EtOH (*diacetate*, m.p. 252°, $[\alpha]_D^{25} -30.1 \pm 2^\circ$ in COMe_2 ; *digitonide*), substance *N*, $\text{C}_{21}\text{H}_{32}\text{O}_4$, $+\text{H}_2\text{O}$, opaque at 120°, m.p. 190°, and anhyd., m.p. 189—191°, $[\alpha]_D^{25} +93.8 \pm 2^\circ$ in abs. EtOH, and a reducing substance (I), $\text{C}_{21}\text{H}_{34}\text{O}_4$ (*diacetate*, m.p. 210—211°). *N* reduces alkaline Ag solutions, has no absorption at 2400 Å., and thus probably contains $\text{CO}\cdot\text{CH}_2\cdot\text{OH}$, but not $\text{C}\cdot\text{C}\cdot\text{CO}$; it may be identical with substance *H* of Mason *et al.* (A., 1937, II, 459). *O* and *J* are forms of *allopregnan-3:17:20-triol*, since with CrO_3 they give *androstane-3:17-dione* and with HIO_4 give *trans-androsterone* (modified prep. from *trans-dehydroandrosterone*), *O* giving also MeCHO . The same products are similarly obtained from *K*, but HIO_4 gives CH_2O instead of MeCHO ; *K* is thus *allopregnan-3:17:20:21-tetraol*. *O* and *J* are stereoisomeric with respect to $\text{C}_{(17)}$ and/or $\text{C}_{(20)}$. *J* is partly isomerised by hot $\text{H}_2\text{SO}_4\text{-H}_2\text{O-MeOH}$ to *allopregnan-3-ol-20-one*. *K* may be identical with the tetraol of Kathol *et al.* (A., 1937, II, 505). (I) probably contains $\text{C}(\text{OH})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$. All these substances are probably physiologically inactive. M.p. are corr.

R. S. C.

Preparation of 23-amino-3:7:12-trihydroxynorcholane from cholic acid. W. T. CALDWELL (J. Amer. Chem. Soc., 1938, 60, 991—993).—The azide, prepared from *Me cholate*, in warm 60% AcOH gives 70% of 23-amino-3:7:12-trihydroxynorcholane, $+\text{2H}_2\text{O}$, m.p. 185—187°, and anhyd., softens at 128—150° [*hydrochloride*, m.p. 306—307°; *platinchloride*, m.p. 230—232° (decomp. from 226°)], not identical with the cholamine of Curtius (A., 1906, i, 400).

R. S. C.

dl-2:2-Dimethylcyclohexylacetic acid. P. S. ADAMSON, A. M. MARLOW, and J. L. SIMONSEN (J.C.S., 1938, 774—776).—2:2-Dimethylcyclohexanone (modified prep.) (2:4-dinitrophenylhydrazones, m.p. 140—142°), $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and Zn in C_6H_6 yield *Et* 1-hydroxy-2:2-dimethylcyclohexylacetate, b.p. 137°/20 mm., converted by KHSO_4 at 180—200° into a mixture,

b.p. 121°/18 mm., of *Et* 2:2-dimethylcyclohexylidenacetate and Δ^6 -cyclohexenylacetate, hydrogenated in EtOH (Pd-C) to *Et* dl-2:2-dimethylcyclohexylacetate, b.p. 122—123°/23 mm., which is hydrolysed by KOH-MeOH to the dl-acid, m.p. $\sim 30^\circ$, b.p. 153°/17 mm. [*p*-phenylphenacyl ester, m.p. 86—87°; *quinine* salt ($+\text{2H}_2\text{O}$), m.p. 97—100° (softens at 90°), $[\alpha]_{5461}^{25} -125.3^\circ$ in CHCl_3]. The *l*-ephedrine salt ($+\text{H}_2\text{O}$), m.p. 90—91°, $[\alpha]_{5461}^{25} -31.1^\circ$ in EtOH, of 1:2:2-dimethylcyclohexylacetic acid, m.p. $\sim 43\text{--}44^\circ$ (softens at 38°), b.p. 149—150°/13 mm., $[\alpha]_{5461}^{25} -14.37^\circ$ in EtOH (*p*-phenylphenacyl ester, m.p. 87—88°, $[\alpha]_{5461}^{25} -2.9^\circ$ in EtOAc), and the *cinchonidine* salt ($+\text{H}_2\text{O}$), m.p. 120—122°, $[\alpha]_{5461}^{25} -86.6^\circ$ in EtOH, of the d-acid (I), m.p. $\sim 37\text{--}40^\circ$, b.p. 150°/13 mm., $[\alpha]_{5461}^{25} +14.1^\circ$ in EtOH (*p*-phenylphenacyl ester, m.p. 87—88°), are used for the resolution. (I) is not identical with the reduction product of *d*-5-keto-2:2-dimethylcyclohexylacetic acid, m.p. 105—107° (cf. A., 1938, II, 289).

A. T. P.

2:2-Dimethylcyclohexylacetic acid. G. H. ELLIOTT and R. P. LINSTEAD (J.C.S., 1938, 776—777; cf. preceding abstract).—2:2-Dimethylcyclohexanone (I), $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and Mg in C_6H_6 yield the *Et* ester, b.p. 136—140°/16 mm., of 1-hydroxy-2:2-dimethylcyclohexylacetic acid, m.p. 99—100°, dehydrated (boiling Ac_2O) to 2:2-dimethylcyclohexylidenacetate (acid, m.p. 91—92°, reduced (H_2 , PtO_2 , AcOH) to the α -hexylacetic acid, new m.p. 47°. (I), $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$, and Mg give poor yields of OH-ester. A. T. P.

Condensations of veratroylformic acid. P. DREYFUSS and C. COCUZZA (Gazzetta, 1938, 68, 95—103).—Veratroylformic acid (I) and PhOMe in AcOH are converted by H_2SO_4 into 3:4:4':4'-tetramethoxytriphenylacetic acid (II), m.p. 163°, also obtained from anisilic acid and veratrole (cf. Jablonski, Diss., Fribourg, 1918). From (II) and H_2SO_4 (cf. *loc. cit.*), or from (I), PhOMe , and 80% H_2SO_4 , 3:4:4':4'-tetramethoxytriphenylcarbinol, m.p. 143.5°, is obtained. 3:4:4':4'-Tetramethoxy-3':3''-dimethyltriphenylacetic acid ($+\text{MeOH}$), m.p. 150°, and α -carbinol, m.p. 147—148.5°, are obtained from $\alpha\text{-C}_6\text{H}_4\text{Me}\cdot\text{OMe}$ and (I) under similar conditions. $p\text{-C}_6\text{H}_4(\text{OMe})_2$ and (I) yield 1:4:6:7-tetramethoxyfluorene-9-carboxylic acid ($+\text{H}_2\text{O}$), m.p. 194°, oxidised by $\text{K}_2\text{Cr}_2\text{O}_7\text{-AcOH}$ to 1:4:6:7-tetramethoxyfluorenone, m.p. 147—148°. Conditions for the formation of fluorenes from diarylcarbinols are discussed. E. W. W.

Preparation of substituted mandelic acids and their bacteriological effects. I. J. L. RIEB-SOMER, J. IRVINE, and R. ANDREWS (J. Amer. Chem. Soc., 1938, 60, 1015—1016).— $\text{CO}(\text{CO}_2\text{Et})_2$, the appropriate hydrocarbon, and SnCl_4 at 0—10° give *Et* α -hydroxy- α -*p*-ethyl-, b.p. 157—160°/4—5 mm., α -*p*-isopropyl-, b.p. 170—174°/4—5 mm., α -*p*-sec-, b.p. 170—176°/4—5 mm., and α -*p*-tert-butyl-, b.p. 183—185°/4—5 mm., and α -2:4:6-trimethyl-phenyl-, b.p. 164—168°/4—5 mm., and α -*p*-tolyl-malonate, b.p. 150—155°/4—5 mm., which, when hydrolysed by 20% KOH and then heated with HCl , yield *p*-ethyl-, m.p. 141—142°, *p*-isopropyl-, m.p. 159.2—160°, *p*-sec-, m.p. 108—109°, and *p*-tert-butyl-, m.p. 149.5—150°, 2:4:6-trimethyl-, m.p. 148—148.5°, and *p*-methyl-mandelic acid, m.p. 145—145.2°, respectively.

Structures are proved by oxidation of the acids. The toxicity of the acids to *B. coli in vitro* is of the same order as that of $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$. R. S. C.

β -Methoxy- β -mesitylacrylonitriles. R. C. FUSON, G. E. ULLYOT, and A. J. GEHRT (J. Amer. Chem. Soc., 1938, 60, 1199—1201).—With Me_2SO_4 -KOH or $\text{MeI}-\text{Ag}_2\text{O}$, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$ (I) gives *cis*- and *trans*-forms, (II), m.p. 66°, and (III), m.p. 82.5—83.5°, of β -methoxy- β -mesitylacrylonitrile. When melted together, (II) and (III) give a 1:1 mol. compound (IV), m.p. 66—68°, also isolable from the methylations. Hot EtOH -conc. HCl rearranges (III) or (IV) into (II). All three, as well as (I), are hydrolysed by H_2SO_4 at 50—55° to 2:4:6-trimethylbenzoylacetylacetamide, m.p. 126—127°. α -Cyanopropion-mesitylene (prep. from $\text{CN}\cdot\text{CHMe}\cdot\text{COCl}$, $\text{C}_6\text{H}_3\text{Me}_3$, and AlCl_3 in CS_2), m.p. 127—128°, with Me_2SO_4 -KOH gives β -cyano- α -methoxy- Δ^2 -propenylmesitylene, m.p. 83—84°. The nitriles show no tendency to polymerise. R. S. C.

β -Phenylnaphthalene. H. E. CARTER and E. J. VAN LOON (J. Amer. Chem. Soc., 1938, 60, 1077—1080).— $\text{OMe}\cdot\text{CHPh}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, m.p. 183—184° and 139—140° (A., 1938, II, 60), with conc. aq. NH_3 at 80—90° give 45—55% of α -amino- β -methoxy- β -phenylpropionic acids, m.p. 253—254° (decomp.) and 235—238° (decomp.), respectively (*Bz* derivatives, m.p. 221—222° and 153—154°, respectively). In boiling 48% HBr the NH_2 -acids (2 mols.) give 2 CO_2 and 80—85% of $2\text{-C}_{10}\text{H}_7\text{Ph}$ and a trace of

$\text{CH}_2\text{Ph}\cdot\text{CH}\langle\begin{smallmatrix} \text{CHPh} \\ \text{O}\cdot\text{CO} \end{smallmatrix}\rangle\text{CO}$ (I); under other conditions a little $\text{CH}_2\text{Ph}\cdot\text{CHO}$ was isolated.

$\text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ (II) and $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}_2$ also give excellent yields of $2\text{-C}_{10}\text{H}_7\text{Ph}$. Boiling $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{OH}$ in 48% HBr gives only 36%, but adding the glycol to the boiling acid gives a 78% yield of $\text{C}_{10}\text{H}_7\text{Ph}$. BzCO_2H in 10% H_2SO_4 or 48% HBr gives 15 and 70%, respectively, of (I) and no $\text{CH}_2\text{Ph}\cdot\text{CHO}$ or $\text{C}_{10}\text{H}_7\text{Ph}$. The mechanism is thus assumed to be a semipinacolic change of (II) to $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{CHX}$ ($\text{X} = \text{O}$ or NH), decarboxylation to $\text{CH}_2\text{Ph}\cdot\text{CHX}$, and condensation to $\text{C}_{10}\text{H}_7\text{Ph}$. R. S. C.

Salts and hydantoin derivatives of β -phenylalanine-*N*-acetic acid. (MISSSES) D. A. HAHN and M. M. ENDICOTT (J. Amer. Chem. Soc., 1938, 60, 1040—1045).—*N*-Carboxymethyl- β -phenylalanine (modified prep.) resembles $\text{NH}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$. It gives *K*, m.p. 205—208° (decomp.), *Na*, m.p. 270° (decomp.), NH_4 , m.p. 201—203° (decomp.), *H* 0.5*Ba*, m.p. >335°, and *Ba* salts, m.p. >335°, a hydrochloride, m.p. 200—201° (decomp.) (gives the free acid when evaporated in H_2O), a carbamyl derivative [*K*₂ salt, $+2\text{H}_2\text{O}$, m.p. 241—242° (decomp.)], and 5-benzylhydantoin-*N*-1-acetic acid, m.p. ($+ \text{H}_2\text{O}$) 110—111° (decomp. 120°) and (anhyd.) 138° (*Na* salt, m.p. 303—304°; *Me*, m.p. 119—120°, and *Et* ester, m.p. 111—112°), the configuration of which is established by methylation ($\text{NaOMe}-\text{MeI}$) to give the *N*-3-*Me* derivative, m.p. 150—151°. R. S. C.

Application of the cyano-ester ring-closure to five- and six-membered rings. R. C. FUSON and

W. COLE (J. Amer. Chem. Soc., 1938, 60, 1237—1239).— $\text{CH}_2(\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et})_2$, b.p. 193—199°/17 mm., and NaCN in hot abs. EtOH give 80—88% of *Et*₂ 1-cyanocyclopentane-1:2-dicarboxylate, b.p. 135—136°/3.5 mm., hydrolysed by conc. HCl to a mixture of *cis*- and *trans*-cyclopentane-1:2-dicarboxylic acid. $(\text{CH}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et})_2$, b.p. 165—167°/3 mm., gives similarly 48—50% of *Et*₂ 1-cyanocyclohexane-1:2-dicarboxylate, b.p. 129—130°/2 mm., hydrolysed (20% HCl) to *cis*- and *trans*-cyclohexane-1:2-dicarboxylic acid. *Et*₂ α' -dibromo-azelate and -sebacate did not give cyclic compounds. R. S. C.

Identification of benzoic, salicylic, and acetyl-salicylic acids.—See B., 1938, 729.

Acetylation reactions with trideuteroacetyl compounds. H. ERLÉNMEYER, H. SÜLLMANN, and H. SCHENKEL (Helv. Chim. Acta, 1938, 21, 401—404).—Subcutaneous injection of *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na}$ and $\text{CD}_3\cdot\text{CO}_2\text{Na}$ led to excretion of *p*- $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na}$ free from *D*, showing that NaOAc is not the acetylating agent (cf. Hensel, A., 1915, i, 627). No exchange occurs when $\text{NHPh}\cdot\text{CO}\cdot\text{CD}_3$ is kept in $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ at 100° for 3 hr. R. S. C.

Alkyl- and dialkyl-amides of *p*-aminobenzoic acid. H. WENKER (J. Amer. Chem. Soc., 1938, 60, 1081).—*p*-Nitrobenz-methyl-, m.p. 217°, -ethyl-, m.p. 151°, -*n*-propyl-, m.p. 103°, -*n*-butyl-, new m.p. 104°, -*n*-amyl-, m.p. 92°, -dimethyl-, m.p. 97°, -diethyl-, m.p. 65°, -*di-n*-propyl-, m.p. 41°, -*di-n*-butyl- and -*di-n*-amyl-amide, oils, *p*-nitrobenz-piperidide, m.p. 121°, *p*-aminobenz-methyl-, m.p. 180°, -ethyl-, an oil (hydrochloride, m.p. 227°), -*n*-propyl-, an oil (hydrochloride, m.p. 223°), -*n*-butyl-, m.p. 99°, -*n*-amyl-, m.p. 98°, -dimethyl-, m.p. 153°, -diethyl-, m.p. 125°, -*di-n*-propyl-, an oil (hydrochloride, m.p. 154°), -*di-n*-butyl-, an oil (hydrochloride, m.p. 141°), and -*di-n*-amyl-amide, an oil (hydrochloride, an oil), and *p*-aminobenz-piperidide, m.p. 162°, are prepared. The higher aminoalkylamides are local anaesthetics. R. S. C.

Derivatives of 1-hydroxy-2-naphthoic acid. IV. Compounds derived from 4-nitro-1-hydroxy-2-naphthoic acid and its methyl ether. S. N. RAO (Proc. Indian Acad. Sci., 1938, 7, A, 261—264; cf. A., 1937, II, 193).—Whereas nitration of $1:2\text{-OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ gives mostly 2:4:1- $\text{C}_{10}\text{H}_5(\text{NO}_2)_2\cdot\text{OH}$ (I), $1:2\text{-OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{Me}$ and HNO_3 (d 1.42) in AcOH at room temp. give *Me* 4-nitro-1-hydroxy-2-naphthoate, new m.p. 159—160°, hydrolysed by 2*N*- NaOH to the corresponding acid (II), new m.p. 212—214° (decomp.) [with hot HNO_3 - AcOH gives (I)], the chloride, m.p. 132—133°, of which yields the *Ph*, m.p. 159—160°, and *Et* ester, m.p. 103—104°, anilide, m.p. 231—232° (decomp.), *o*-, m.p. 201—202° (decomp.), *m*-, m.p. 236—237°, and *p*-toluidide, m.p. 258—259°. $1:2\text{-OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{Me}$ with HNO_3 - AcOH at 100° gives *Me* 4-nitro-1-methoxy-2-naphthoate, m.p. 110—111°, and thence the corresponding acid, new m.p. 196—197° [with $\text{HI}-\text{AcOH}$ gives (II)]; chloride, m.p. 103—104°; *Ph*, m.p. 114—115°, and *Et* ester, m.p. 101—102°; anilide, m.p. 170—171° (decomp.); *o*-, m.p.

175—176°, *m*-, m.p. 138—140°, and *p*-toluidide, m.p. 164—165°]. R. S. C.

Acylation of aromatic amino-sulphonic acids.
III. 2-Hydroxy-3-naphthoyl derivatives of anilinesulphonic acids, and derived azo-dyes. N. N. VOROSCHCOV and N. D. GENKIN (J. Gen. Chem. Russ., 1938, 8, 357—365).—The *o*-, *m*-, and *p*-sulphoanilides of 2-hydroxy-3-naphthoic acid (I) have been prepared from (I), *o*-, *m*-, and *p*-NH₂·C₆H₄·SO₃H, and PCl₅ in C₅H₅N. The Fe^{II}, Cu^{II}, Ni^{II}, Pb^{II}, and Cr^{III} salts, and the benzeneazo-derivatives of the sulphanilides are described. R. T.

Reducto-dehydrocholic acid.—See B., 1938, 731.

Diphenic acid hydrazides. R. A. LABRIOLA (Anal. Asoc. Quím. Argentina, 1937, 25, 121—131).—Diphenic anhydride with N₂H₄·H₂O yields diphenic acid monohydrazide (I), m.p. 183° (decomp.) (lit. 164°), which loses H₂O at 200°/vac. to give the secondary hydrazide, m.p. 305° (lit. 250°) (Ac₂ derivative, m.p. 185—186°), also obtained from (C₆H₄·COCl)₂ or Me diphenate (II) and N₂H₄·H₂O (2 mols.). Excess of N₂H₄·H₂O with (II) yields the dihydrazide, m.p. 215—216°, also obtained (both methods) from the Et ester. (I) with H₂SO₄ yields fluorenone-4-carboxylic acid. HNO₂ converts (I) into the azide, decomp. 58—60°; in EtOH at 96° this gives phenanthridone and 2-hydroxydiphenyl-2'-carboxylic acid lactone. F. R. G.

Partial degradation of azafrin by potassium permanganate. P. KARRER, H. OBST, and U. SOLMSEN (Helv. Chim. Acta, 1938, 21, 451—453).—Oxidation of azafrin Me ester (in CHCl₃) by aq. KMnO₄-NaHCO₃ gives products of low mol. wt., but azafrin gives readily, apo-1-azafrinal,

$$\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CMe}(\text{OH}) \\ \text{CH}_2 \text{---} \text{CMe}_2 \end{array} \text{C}(\text{OH}) \cdot [\text{CH} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CH}]_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CHO},$$
m.p. 171° [sharp absorption (4310 Å.) only in light petroleum; *oxime*, m.p. 185° (decomp.) (absorption detailed)]. R. S. C.

α-Citraurin, a degradation product of xanthophyll. P. KARRER, H. KOENIG, and U. SOLMSEN (Helv. Chim. Acta, 1938, 21, 445—448).—Aq. KMnO₄ containing Na₂CO₃ oxidises xanthophyll diacetate in C₆H₆ to α-citraurin,

$$\text{OH} \cdot \text{CH} \begin{array}{c} \text{CH} = \text{CMe} \\ \text{CH}_2 \text{---} \text{CMe}_2 \end{array} \text{CH} \cdot [\text{CH} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CH}]_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CHO},$$
m.p. 153°, [α]_D²⁰ +372°, [α]_D²⁰ +328°, [α]_D²⁰ +263°, [α]_D²⁰ +219° in C₆H₆ (*oxime*, m.p. 148°), and a little β-citraurin (not obtained pure). The absorption (defined) of the α-compound resembles that of α-apo-2-carotenal. R. S. C.

β-Citraurin, a degradation product of zeaxanthin. P. KARRER, A. RÜEGGER, and U. SOLMSEN (Helv. Chim. Acta, 1938, 21, 448—451).—The isolation of the aldehyde,

$$\text{HO} \cdot \text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \text{---} \text{CMe}_2 \end{array} \text{C} \cdot [\text{CH} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CH}]_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CHO},$$
now termed β-citraurin [*oxime*, m.p. 192—194° (previous sintering)] by KMnO₄-oxidation of zeaxanthin acetate is described (cf. A., 1937, II, 378, 502). R. S. C.

***m*-Dimethylaminobenzaldehyde.** II. W. COCKER, J. O. HARRIS and (in part) J. V. LOACH (J.C.S., 1938, 751—753).—*m*-NO₂·C₆H₄·CH(OMe)₂ and Na₂S in aq. HCl give the *m*-NH₂-analogue, which with Me₂SO₄ and 7% Na₂CO₃ (in Et₂O), followed by hot KOH, yields *m*-NMe₂·C₆H₄·CHO (I) [2:4-dinitrophenylhydrazone hydrochloride, m.p. 231° (decomp.); *platinichloride* (+2H₂O), m.p. 167—168° (decomp.); *azine*, m.p. 153—154°; 6-*NO*-derivative, m.p. 129.5—130°]. (I), NPhMe₂ (NPhEt₂), and anhyd. ZnCl₂ give *leuco-bases*, m.p. 149—149.5° (72—73.5°), readily oxidised by PbO₂; (I) does not react with KCN or NaHSO₃. *o*-NO₂·C₆H₄·CH(OMe)₂ similarly affords *o*-NMe₂·C₆H₄·CHO [*semicarbazone*, m.p. 224—225° (decomp.)]. *Ph o*- and *m*-dimethylaminostyryl ketones have m.p. 66—67° and 108—109°, respectively. A. T. P.

Synthesis of 4-methylpyrogallolaldehyde [2:3-dihydroxy-4-methoxybenzaldehyde]. F. MAUTHNER (J. pr. Chem., 1938, [ii], 150, 257—260; cf. A., 1936, 1109).—2-Hydroxy-3-methoxybenzaldehyde is converted by H₂O₂ in alkaline solution into pyrogallol 1-Me ether (I), transformed by Zn(CN)₂ and HCl in Et₂O and subsequently by boiling H₂O into 2:3-dihydroxy-4-methoxybenzaldehyde (II), m.p. 118—119° (regarded previously as the 3:4:2-compound); its constitution is established by its conversion by Ac₂O and NaOAc into 8-hydroxy-7-methoxycoumarin, m.p. 169—170°. CH₂(CO₂H)₂, NH₂Ph, and (II) in EtOH afford 5:6-dihydroxy-4-methoxycinnamic acid, m.p. 264—265°. (I) and AcCl afford the diacetate, converted by AlCl₃ in PhNO₂ into 2:3-dihydroxy-4-methoxyacetophenone, m.p. 132—133°. H. W.

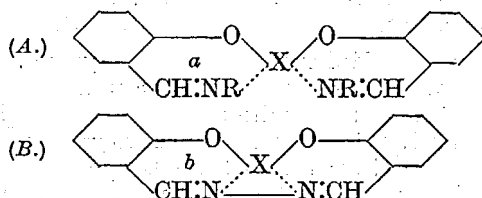
C-Alkylresorcinols. III. Direct synthesis of rhizonaldehyde. R. C. SHAH and B. V. SAMANT (Proc. Indian Acad. Sci., 1938, 7, A, 266—268; cf. A., 1936, 1245).—Rhizonaldehyde is obtained in moderate yield from oreylaldehyde, MeI, and KOH in hot MeOH. R. S. C.

Ionisation constants of isomeric hydroxy-naphthaldehydes. Structure of naphthalene nuclei. R. T. ARNOLD and J. SPRUNG (J. Amer. Chem. Soc., 1938, 60, 1163—1164).—*k* × 10¹⁰ are found as follows in 0.05M solution in 50 wt.-% aq. EtOH: α- 0.1 and β-C₁₀H₇·OH 0.1, 2:1- 53.7, 1:2- 138, and 3:2-OH·C₁₀H₆·CHO 1.175. The vals. for the aldehydes indicate that the double linking is largely between C₍₁₎ and C₍₂₎. R. S. C.

Stereochemistry of anils. V. DE GAOUCK and R. J. W. LE FÈVRE (J.C.S., 1938, 741—745).—Dielectric consts. and density measurements of C₆H₆ solutions of the two forms of salicylideneaniline (I) (Anselmino, A., 1907, i, 913) show identical vals.; one form only, m.p. 86.5°, of 5-bromosalicylidene-*o*-toluidine (cf. A., 1933, 393) could be isolated. Thus common Schiff's bases appear to occur in one form only. Dipole moments of (I), its 5-Br-derivative, and CHR·NR' (R = R' = Ph; R = *p*-C₆H₄Cl, R' = Ph, *p*-C₆H₄Me, and *p*-C₆H₄Cl; R = *o*-C₆H₄·OMe, R' = Ph; R = *o*-C₆H₄·OH, R' = *m*-C₆H₄Me) indicate that R and R' are in *trans*-relation to C·N (cf. A., 1938, II, 63). The possibility that phototropic changes among

the anils involves configurational inversions of the *cis* \rightleftharpoons *trans* type is not supported. A. T. P.

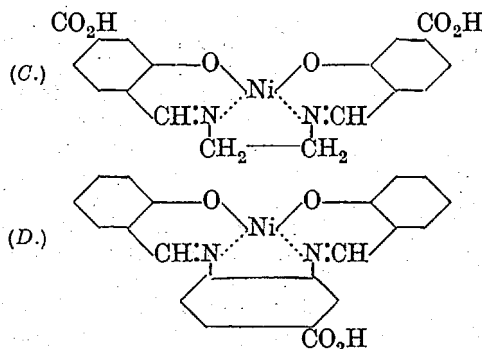
Stereochemistry of spiran-like complex salts. Cotton effect. P. PFEIFFER, W. CHRISTELEIT, T. HESSE, H. PFITZNER, and H. THIELERT (J. pr. Chem., 1938, [ii], 150, 261—316; cf. A., 1938, II, 62).—Attempts to resolve suitable compounds of the type (A) or (B) into optical antipodes or, after introduction



of an asymmetric C, to obtain evidence of isomerism were unsuccessful. Although absent from the fundamental Schiff's bases, a pronounced Cotton effect is observed in the visible portion of the spectrum of the optically active complex salts which contain a chromophoric metallic atom. The Cotton effect is observed in both bicyclic and tricyclic complex salts and a subsidiary valency ring of the second type (with two subsidiary valencies) need not be present. The position of the asymmetric C relative to the metallic atom is not very material for the incidence of the Cotton effect. It is immaterial in principle whether the asymmetric C is present in a C chain united to the N of the central group N(O)X(O)N or in the nucleus of the OH-aldehydic component. It is also unimportant whether the chromophoric metal atom and the asymmetric C are separated from one another by one or by several atoms. For the development of the Cotton effect it appears necessary that the asymmetric C should be accompanied by a further asymmetric centre, i.e., by the chromophoric metallic atom (Cu, Ni, V). The two subsidiary valency rings are not therefore in a single plane but more or less inclined to one another so that the four groups around the metallic atom are spatially (tetrahedrally) arranged. In the absence of asymmetric C a plane arrangement appears to be established. This configuration is considered to be dynamic, not static, so that after introduction of asymmetric C the position of equilibrium occurs when the planes of the two rings are inclined to one another. The necessity of recognising the existence of subsidiary valencies in addition to Kekulé's main valencies in many org., particularly metallic, compounds is again established since the incidence of the Cotton effect is explicable only if the compounds are regarded as complex and not as ordinary salts.

The following Schiff's bases are described: salicylaldehyde-*d*-bornylimine, m.p. 62°, $[M]_{589}^{23} + 250^\circ$ in MeOH (in all cases $[M]$ for many vals. of λ is recorded), *d*-neobornylimine, m.p. 36°, $[M]_{589}^{22} - 396^\circ$ in MeOH, *d*(-)-propylenedi-imine (non-cryst.), β -methyltetramethylenedi-imine, m.p. 67°, $[M]_{589}^{24} - 256^\circ$ in MeOH, *l*-1-diphenylethylenedi-imine, m.p. 148°, $[M]_{589}^{18} + 139^\circ$ in MeOH, *l*-1:3-diaminocis-1:2:2-trimethylcyclopentane, m.p. 157—158°, $[M]_{589}^{20} + 112^\circ$ in MeOH, and *cis*-bisaminomethylcamphocean, m.p. 118°, $[M]_{589}^{21} - 443^\circ$ in C_6H_6 ; *d*-formylcamphorethylenedi-imine,

m.p. 212—213°, $[M]_{589}^{19} + 1120^\circ$ in MeOH (Bz derivative, m.p. 175—176°); *l*-formylcamphorethylenedi-imine, m.p. 214—215°; *d*-formylcamphor-*d*(-)-propylenedi-imine, m.p. 195—196°, $[M]_{589}^{18} + 1225^\circ$ in MeOH; *d*-formylcamphor-*dl*-propylenedi-imine, m.p. 212—213°, $[M]_{589}^{18} + 1120^\circ$ in MeOH; *l*-formylcamphor-*d*(-)-propylenedi-imine, m.p. 178—181°, $[M]_{589}^{21} - 1135^\circ$ in MeOH; *dl*-formylcamphor-*d*(-)-propylenedi-imine, m.p. 170°, and *l*(+)-propylenedi-imine, $[M]_{589}^{17} + 280^\circ$ in MeOH. Attempts to resolve the



acid (C) were unsuccessful by reason of lack of crystallising power of the salts. (D) could not be resolved by *d*-coniine or by active triethylenediaminecobaltic bromide whilst its *l*-menthyl ester appears inactive in 0.1% solution. Ni salicylaldehyde-*r*-propylenedi-imine and the complex Cu salt of *l*(+)-valine could not be obtained in isomeric forms. Indications of isomerism are not obtained with Cu salicylaldehyde-*d*(-)-propylenedi-imine (I), $[M]_{589}^{19} + 615^\circ$ in MeOH, *l*(+)-propylenedi-imine (II), $[M]_{589}^{19} - 480^\circ$ in MeOH, Ni salicylaldehyde-*d*(-)-propylenedi-imine, $[M]_{589}^{22} + 3190^\circ$ in MeOH, or *l*(+)-propylenedi-imine, $[M]_{589}^{22} - 3150^\circ$ in MeOH. All these salts show a very pronounced Cotton effect. Very characteristic curves are also shown by Cu salicylaldehyde-*cis*-1:2:2-trimethylcyclopentane-1:3-di-imine, $[M]_{589}^{18} + 2390^\circ$ in MeOH, and Ni salicylaldehyde-*cis*-1:2:2-trimethylcyclopentane-1:3-di-imine, $C_{22}H_{24}O_2N_2Ni$, $[M]_{589}^{20} + 325^\circ$ in MeOH [compound $2C_{22}H_{24}O_2N_2Ni \cdot Ni(OAc)_2$], and by the Cu salt of the *trans*-diamine. Anomalous dispersion is also exhibited by Co salicylaldehyde-*d*(-)-propylenedi-imine, $[M]_{589}^{23} - 3730^\circ$ in MeOH, *l*(+)-propylenedi-imine, $[M]_{589}^{23} + 4070^\circ$ in MeOH, and by vanadyl salicylaldehyde-*d*(-)-propylenedi-imine (also +EtOH), $[M]_{589}^{22} + 2137^\circ$ in EtOH, and *l*(+)-propylenedi-imine (also +EtOH), $[M]_{589}^{22} - 2007^\circ$ in EtOH. Vanadyl salicylaldehyde-*cis*-1:2:2-trimethylcyclopentane-1:3-di-imine, $[M]_{589}^{19} - 797^\circ$ in MeOH, and *l*-diphenylethylenedi-imine, $[M]_{589}^{20} + 1552^\circ$ in MeOH, are described. The theory of the Cotton effect requires the metallic atom to be a chromophoric centre; as expected, therefore, normal rotatory dispersions are shown by Zn salicylaldehyde-*d*(-)-propylenedi-imine, $[M]_{589}^{20} + 1280^\circ$ in MeOH, and *l*(+)-propylenedi-imine, $[M]_{589}^{20} - 1330^\circ$ in MeOH. The non-dependence of the Cotton effect on the proximity of metallic atom and asymmetric C is established by the observed anomalous rotatory dispersion of Cu salicylaldehyde-*d*- β -methyltetramethylenedi-imine, $[M]_{589}^{24} - 316^\circ$ in C_6H_6 , and the corresponding Ni compound, $[M]_{589}^{21} - 6790^\circ$ in C_6H_6 , to which the

Cu, $[M]_{589}^{19} - 6680^\circ$ in C_6H_6 , and *Ni* (anhyd. and $+H_2O$), $[M]_{589}^{21} + 3900^\circ$ in C_6H_6 , salts of the Schiff base from $o-OH \cdot C_6H_4 \cdot CHO$ and *cis*-bisaminomethylcamphocean bear close resemblance. It is not necessary that the asymmetric centre and chromophoric atom should be in the same subsidiary valency ring since a pronounced Cotton effect is given by *Cu salicylaldehyde-l-sec-butylimine*, $[M]_{589}^{20} - 1978^\circ$, -d-, $[M]_{589}^{20} - 1690^\circ$ in MeOH, and -l-, $[M]_{589}^{20} + 1830^\circ$ in MeOH, -phenylethylimine, and by *Cu salicylaldehyde-d-bornylimine*, m.p. 202° , $[M]_{589}^{21} + 6510$. *Cu formylcamphor*, $[M]_{589}^{24} + 300^\circ$ in MeOH (also +1 mol. of dioxan), but not the corresponding *Ni* salt, $[M]_{589}^{23} + 1000^\circ$ in MeOH, shows anomalous rotatory dispersion. *Cu d- (anhyd. and monohydrate)*, $[M]_{589}^{17} - 725^\circ$ in Bu^oOH and *Cu l- (monohydrate and anhyd.)*, $[M]_{589}^{20} + 810^\circ$ in Bu^oOH -formylcamphorethylenedimine and the corresponding *Ni d- (anhyd. and trihydrate)*, $[M]_{589}^{17} - 1985^\circ$ in MeOH and l-salts (anhyd. and trihydrate, $[M]_{589}^{15.5} + 2350^\circ$ in MeOH) show a pronounced Cotton effect. These salts are closely resembled by *Cu d-*, $[M]_{589}^{18} - 295^\circ$ in Bu^oOH , and -l-, $[M]_{589}^{14.5} + 725^\circ$ in Bu^oOH , -formylcamphor-dl-propylenedimine. *Cu dl-formylcamphor-d(-)-*, $[M]_{589}^{15} + 1635^\circ$ in Bu^oOH , and -l(-)-, $[M]_{589}^{15.5} - 1675^\circ$ in Bu^oOH , -propylenedimine are very similar to (I) and (II). *Cu d-formylcamphor-l(+)-propylenedimine*, $[M]_{589}^{16} - 2010^\circ$ in Bu^oOH , and *Cu l-formylcamphor-d(+)-propylenedimine*, $[M]_{589}^{23} + 2426^\circ$ in Bu^oOH , show very pronounced Cotton effect which is less marked with *Cu d-formylcamphor-d(-)-propylenedimine*, $[M]_{589}^{18} + 970^\circ$ in Bu^oOH , and *Cu l-formylcamphor-l(+)-propylenedimine*, $[M]_{589}^{16} - 830^\circ$ in Bu^oOH . *Cu d-benzoylcamphor*, $[M]_{589}^{18} + 915^\circ$ in MeOH, and *Ni d-benzoylcamphor* (also $+2C_5H_5N$), $[M]_{589}^{19} + 1390^\circ$ in MeOH, do not show the Cotton effect. *Ferryl salicylaldehyde-d(-)-propylenedimine* is too deeply coloured to permit accurate determination of α in MeOH. *Fe^{III} d-formylcamphor* has $[M]_{589}^{18} + 2950^\circ$ in Bu^oOH . *Uranyl salicylaldehyde-d(-)-propylenedimine* (+1EtOH and solvent-free, $[M]_{589}^{21} + 57^\circ$ in EtOH), and -l-diphenylethylenedimine are described.

H. W.

Action of sodium phenylacetylene on $\alpha\beta$ -unsaturated esters. D. E. Worrall (J. Amer. Chem. Soc., 1938, 60, 1266).— $CPh:CNa$ and Et or Me cinnamate in warm Et_2O give *cinnamoylphenylacetylene*, m.p. $140-141^\circ$, the unsaturated groups of which hinder CO-reactivity; it gives tars under vigorous conditions. The ketone acts as enol, e.g., with Grignard reagents.

R. S. C.

Alkylation of hydroxymethylenedeoxybenzoin. A. H. BLATT (J. Amer. Chem. Soc., 1938, 60, 1164-1167).—The mode of methylation of a hydroxymethyleneketone depends on the conditions and on the ketone and cannot be foretold. Contrary to Jörisen (Diss., Basel, 1893) $COPh \cdot CPh \cdot CH \cdot OH$ (I) with $HCl-MeOH$ at room temp. or with MeI and $NaOMe$ in hot MeOH gives $COPh \cdot CH_2Ph$. Short treatment with warm ROH -conc. HCl and keeping for about 24 hr. gives γ -keto- $\beta\gamma$ -diphenylpropaldehyde Me_2 , m.p. $102-103^\circ$, Et_2 , m.p. $68-69^\circ$, and $(CH_2Ph)_2$ acetal, m.p. $69-70^\circ$; MeOH-conc. HCl similarly converts the Et_2 or $(CH_2Ph)_2$ into the Me_2 acetal, the structure of

which is proved by slow hydrolysis by $NaOH$ to $COPh \cdot CH_2Ph$ and by conversion by $NHPh \cdot NH_2$ in $AcOH$ into 1:4:5-triphenylpyrazole. With $MeI-NaOMe$ traces of $COPh \cdot CPh \cdot CH \cdot OMe$ and $COPh \cdot CHPh \cdot Me$ are formed. With CH_2N_2 in $CHCl_3$, (I) gives *methoxymethylenedeoxybenzoin*, m.p. $130-131^\circ$, which is rapidly hydrolysed by acid and thus gives the Me_2 acetal when warmed in $HCl-MeOH$ and slowly develops a colour in $FeCl_3$ -aq. EtOH unless $NaOAc$ is present.

R. S. C.

Addition of diphenylketen to styrene. E. BERGMANN and (MRS.) O. BLUM-BERGMANN (J.C.S., 1938, 727-729).—The addition product of $CPh_2 \cdot CO$ and $CHPh \cdot CH_2$ is 2:2:3-triphenylcyclobutan-1-one, which with $NaOH-EtOH$ yields $\beta\gamma$ -triphenylbutyric acid, m.p. 178° [Me (I) and Et (II), m.p. 83° , esters], identical with the acid of Staudinger and Rheiner (A., 1924, i, 295). α -Methyldeoxybenzoin and $MgPhBr$ give $\alpha\beta$ -triphenylpropan- α -ol, m.p. $92-93^\circ$, converted by MeI and K in xylene into the *Me ether*, m.p. $98-99^\circ$, which when treated successively with Na in Et_2O for several weeks and with CO_2 at 0° gives $\alpha\beta$ -triphenylbutyric acid, m.p. 158° . In the prep. of (I) and (II) from $CHNaPh_2$ and $CHPh \cdot CH_2 \cdot CO_2Alk$, some *dibenzhydrylstyrylcarbinol*, (?), m.p. 172° , is obtained. Dimeric diphenylketen (cf. Langenbeck, A., 1928, 762) may be 2:3-diketol:4-diphenyl-1:2:3:4-tetrahydronaphthalene.

A. T. P.

Relative oxidation-reduction reactivities of ketones and aldehydes and applications in synthesis. H. ADKINS and F. W. COX (J. Amer. Chem. Soc., 1938, 60, 1151-1159).—The polarographic reduction potentials of 57 aldehydes, ketones, diketones, and other substances are determined. Some substances have two such potentials. In many cases the potentials in acid and alkaline solution differ. $COMe_2$, $CH_2(COMe)_2$, cyclopentanone, and triacetoneamine have immeasurably high potentials, i.e., >2.1 v. Unsaturated and aryl groups lower the potential. Diketones have low potentials, quinones still lower. The behaviour of Bz_2 and benzoin indicates the following reactions: $Bz_2 \rightleftharpoons ^-O \cdot CR \cdot CR \cdot O^+ \xrightarrow{0.4v} ^-O \cdot CR \cdot CR \cdot O^-$ (I) $\xrightarrow[NMe_2 \cdot OH]{0.7v} CH_2R \cdot COR \xrightarrow{1.4v} CH_2R \cdot CHR \cdot OH$; (I) $\xrightarrow[NH_4Cl]{0.7v} (CHR \cdot OH)_2 \xrightarrow[NMe_2 \cdot OH]{1.4v} COR \cdot CHR \cdot OH \rightleftharpoons OH \cdot CR \cdot CR \cdot OH$ (I). Potentials of substances sometimes vary according to the nature of other substances present. The method of determining by means of the polarograph the ratio and concns. of two ketones when present together in solution is discussed. Equilibria, $COR_2 + CHR'_2 \cdot OH \rightleftharpoons COR'_2 + CHR_2 \cdot OH$, brought about by $Al(OBu')_3$ at $40-100^\circ$ are investigated by the polarograph. Measurements involving $COPhMe$ are vitiated by simultaneous formation of dypnone, $COPh \cdot CH \cdot CPhMe$. Equilibrium, $COPh_2 + CHPhR \cdot OH \rightleftharpoons CHPh_2 \cdot OH + COPhR$, is reached much faster when $R = Pr^a$ than when $R = Pr^b$ and leads to 67% of $COPhPr^a$ and only 54% of $COPhPr^b$. *sec*-Alcohols, which give ketones having high reduction potentials, e.g., Pr^bOH , are the best reducing agents and reduce many ketones almost quantitatively to alcohols. Choice of a suitable ketone as oxidising agent is less clear cut and the reaction would be

materially favoured by removal of one product; quinones, α -OH-ketones, and α -diketones having reduction potentials of ≤ 1 v., are probably the best oxidising agents. The prep. of $\text{Al}(\text{OBu}^n)_3$ is described. $\text{Al}(\text{OBu}^n)_3$ converts COPhMe in dioxan into dypnone in 30% yield, and other ketones give 80% yields of similar products. R. S. C.

Action of mixed organo-magnesium compounds on the phenylhydrazones of trialkylacetophenones. P. GRAMMATICAKIS (Compt. rend., 1938, 206, 1307—1309; cf. A., 1937, II, 248).—Prolonged heating of the phenylhydrazone, m.p. 94° (1 mol.), of $\text{COPh}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Ph}$ (I) with MgEtBr or MgMeI (6 mols.) at 116° affords (I), its imine and anil, and NH_2Ph . The phenylhydrazones, m.p. 92° and b.p. 160°/1 mm., of COPhBu^n and $\text{COPh}\cdot\text{CMe}_2\text{Bu}^n$, respectively, react similarly. A probable mechanism for the reaction is described. J. L. D.

Pyrolysis of organomagnesium compounds. I. New agent for reduction of benzophenone. D. B. CLAPP and R. B. WOODWARD (J. Amer. Chem. Soc., 1938, 60, 1019—1020).—At 220°/0.5 mm. MgEtI gives C_2H_4 and a mixture of H_2Mg and MgI_2 , which reacts vigorously with H_2O and alcohols, and reduces COPh_2 in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$ to $\text{CHPh}_2\cdot\text{OH}$ in 66% yield. The pyrolysis product of MgMeI reacts with H_2O , but does not reduce COPh_2 . R. S. C.

Lignans. Correction of some published data on [products from] olivil. B. L. VANZETTI and P. DREYFUSS (Gazzetta, 1938, 68, 87—91).—The original m.p. (A., 1934, 1099) of 3-methoxy-4-ethoxy-6-veratroylbenzoic acid, 2:3:6-trimethoxy-7-ethoxyanthraquinone (I), and 3:4:4'-trimethoxy-3'-ethoxy- (II) and 3:4:3'-trimethoxy-4'-ethoxy-benzophenone (III) are confirmed (cf. Omaki, J. Pharm. Soc. Japan, 1937, 57, 22, 89), and the new m.p. 139—140° (corr.) and 126—127° (corr.) obtained for the oximes of (II) and (III), respectively. Omaki's supposed (I) is a partly dealkylated product. E. W. W.

Pyrene series. II. K. DZIEWOŃSKI and P. TRZESIŃSKI (Bull. Acad. Polonaise, 1937, A, 579—582; cf. A., 1937, II, 285).—Pyrene, EtCOCl , and AlCl_3 in PhNO_2 at 18—23° give 3-propionylpyrene, m.p. 84—85° (picrate, m.p. 158.5°), the orientation of which is proved by conversion of its oxime, m.p. 192—193°, by $\text{HCl}\cdot\text{Ac}_2\text{O}$ into 3-propionamidopyrene, m.p. 231—232°, hydrolysed to 3-aminopyrene. With MgMeI the ketone gives 3- β - Δ^a -butenylpyrene, m.p. 75—76° (picrate, m.p. 140—141°). R. S. C.

Formation of the indene nucleus. III. (MRS.) O. BLUM-BERGMANN (J.C.S., 1938, 723—726).—*p*-Anisoylphenylcarbinol (I) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ afford α -*diphenyl*- β -*p*-anisylpropane- β -*γ*-diol (II), m.p. 155—156.5°, and some $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ (?) (III), m.p. 134—135.5°. (II) and AcCl give an *Ac* derivative, m.p. 178—179.5°, and 1-phenyl-2-*p*-anisylindene (IV), m.p. 188—188.5°, isomerised by $\text{Pr}^n\text{OH}\cdot\text{EtOH}\cdot\text{NaOEt}$ to 3-phenyl-2-*p*-anisylindene, m.p. 120—121°, giving the same CHPh derivative, m.p. 192—193°, as does (IV) (Koelsch, A., 1936, 1255). Benzoyl-*p*-anisylcarbinol (V), m.p. 88—89° (cf. Luis, A., 1932, 1251) (oxime, m.p. 121—122.5°), is isomerised

K (A., II.)

by boiling AcOH to (I). (V) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ yield α -*diphenyl*- γ -*p*-anisylpropane- β -*γ*-diol (VI), m.p. 161—163°, which with P_2O_5 in C_6H_6 , or AcCl , gives no indene derivative, but (III) and a compound, m.p. 48—49.5°, isomeric with (VI). 3-Phenyl-2-methylindene and MgPhBr give a carbinol, converted by $\text{HCl}\cdot\text{MeOH}$ into 1-methoxy-1:3-diphenyl-2-methylindene, m.p. 71—72.5°, which with Na , followed by MeI , gives 1:3-diphenyl-2:3-dimethylindene, m.p. 68.5—69.5°, hydrogenated ($\text{Pd}\cdot\text{BaSO}_4$, Pr^nOH) to 1:3-diphenyl-2:3-dimethylhydrindene, m.p. 97.5—98.5°. *cis*-+*trans*- α - β -Dimethylcinnamic acids and AlCl_3 in C_6H_6 (room temp., 7 days) afford 2:3-dimethylindene, some β -phenyl-, m.p. 132—133.5°, and β -*diphenyl*- α -methylbutyric acid, m.p. 124—126°; the chloride, b.p. 188—189°/17 mm., of the last is converted by AlCl_3 in CS_2 into 3-phenyl-2:3-dimethylhydrindone, b.p. 189—192°/16 mm., which does not react with MgPhBr . 3-Phenyl-3-methylhydrindone (cf. A., 1932, 273) and PhCHO in $\text{EtOH}\cdot\text{KOEt}$ at 0° give the 2-*CHPh* derivative, m.p. 121—122°, reduced (Clemmensen) to 1-phenyl-2-benzyl-1-methylhydrindene, m.p. 117—118.5°. A. T. P.

2:3:6:7-Tetramethoxyfluorene and some of its derivatives. P. DREYFUSS (Gazzetta, 1938, 68, 92—95).—Veratroylformic acid and veratrole in 80% H_2SO_4 yield 2:3:6:7-tetramethoxyfluorene-9-carboxylic acid (I) (+ H_2O), decomp. >200° to (II) and (III) (below). In boiling Ac_2O , (I) gives a substance, m.p. 285° (decomp.), and, in quinoline at 240°, 2:3:6:7-tetramethoxyfluorene (II), m.p. 196°. With $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH , (I) yields 2:3:6:7-tetramethoxyfluorenone (III), m.p. 203°, also obtained (Oliverio, A., 1936, 1256; cf. Dreyfuss, *ibid.*) by the benzilic transformation of 2:3:6:7-tetramethoxyphenanthraquinone, followed by oxidation, and identified with the "red substance" produced on aerial oxidation of veratrilic acid (A., 1927, 462). Aerial oxidation of an alkaline solution of (I) also gives (III). With KMnO_4 in aq. Na_2CO_3 , (I) gives (III) and a substance, $\text{C}_{17}\text{H}_{16}(\text{or } 18)\text{O}_6$, m.p. 258—259°. E. W. W.

Union of aryl nuclei. III. 3'-Hydroxymesobenzanthrone. I. M. HEILBRON, D. H. HEY, and R. WILKINSON (J.C.S., 1938, 699—701; cf. A., 1938, II, 93).—2- $\text{C}_{10}\text{H}_7\cdot\text{OMe}$ and diazotised *Me* anthranilate in CHCl_3 give 2-methoxy-1-phenyl-naphthalene-2'-carboxylic acid, m.p. 218—220° (*Me*, m.p. 85—86°, and *Et* ester, m.p. 83—84°), cyclised by PCl_5 in C_6H_6 followed by AlCl_3 to 3'-hydroxymesobenzanthrone (*Me* ether, m.p. 147—148°), identical with a specimen prepared by oxidation (KMnO_4) of 1:8-phthaloyl- β -naphthol. A. Lr.

trans-3-Acetonyl-2:2-dimethylcyclobutane-1-carboxylic acid: an isomeride of pinonic acid. P. C. GUHA and P. L. N. RAO (Current Sci., 1938, 6, 451).—Partial esterification of *trans*-pinic acid, or partial hydrolysis of its *Et* ester, gives *Et* *trans*-2:2-dimethyl-3-carboxymethylcyclobutane-1-carboxylate, b.p. 158—160°/5 mm.; the acid chloride of which, b.p. 118°/4.5 mm., with ZnMeI yields the *Et* ester, b.p. 118—119°/5 mm. (semicarbazone, m.p. 134°), of the 3-acetonyl-1-carboxylic acid (semicarbazone, m.p. 186°). This acid differs from *cis*- and *trans*-pinonic acid, and

from orthodonic acid, which must therefore be the *cis*-form. A. Lr.

Semicarbazone and thiosemicarbazone of *p*-methoxyphenylpyruvic acid. Corresponding dihydroxytriazine and hydroxythioltriazine. M. GIRARD (Compt. rend., 1938, 206, 1303—1305; cf. A., 1928, 775).—The semicarbazone, decomp. 178° (block), of *p*-methoxyphenylpyruvic acid (I) when boiled in a slightly alkaline solution affords 3:5-dihydroxy-6-*p*-methoxybenzyl-1:2:4-triazine (II), m.p. 215°. The thiosemicarbazone, m.p. 174° (decomp.), of (I) similarly treated affords 5-hydroxy-3-thiol-6-*p*-methoxybenzyl-1:2:4-triazine, m.p. 177°, converted by NaOBr into (II). J. L. D.

β -Arylglutaconic acids. IV. C-Acetylation of β -arylglutaconic anhydrides. Derivatives of α -aceto- β -arylglutaconic acids. G. R. GOGTE (Proc. Indian Acad. Sci., 1938, 7, A, 214—228).— β -*p*-Anisylglutaconic anhydride and $\text{AcCl}-\text{C}_6\text{H}_5\text{N}$ or the acid and $\text{Ac}_2\text{O}-\text{NaOAc}$ give α -aceto- β -*p*-anisylglutaconic anhydride (I), m.p. 132° (cf. Limaye and Bhawe, A., 1934, 890, who formulate it as a glutaconyl-acetic acid); with dil. HCl it gives β -*p*-anisylpropylene. (I) refluxed with H_2O or NaOH affords δ -keto- β -*p*-anisyl- Δ^{α} -hexenoic acid (II), m.p. 125° (decomp.) [conc. HCl gives a lactone (III), m.p. 112° (structure discussed), hydrolysed (NaOH) to (II)], decarboxylated at 130—140° to δ -keto- β -*p*-anisyl- Δ^{α} -pentene (IV), new m.p. 50° [semicarbazone, m.p. 188—189° (decomp.)], not oxidised to *p*-methoxy- β -methylcinnamic acid (V) (cf. *loc. cit.*), but converted by NaOBr into anisic acid and by 10% NaOH into *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{COMe}$ (VI) [semicarbazone, new m.p. 189—190° (decomp.)]. (I) refluxed with EtOH yields the α -Et₁ ester (VII), m.p. 138° (decomp.) [converted by conc. HCl into the lactone (VIII), *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}(\text{CO}_2\text{Et})\cdot\text{CMe} \end{smallmatrix} \text{O}$, m.p. 106°; semicarbazone, m.p. 154° (decomp.)], decarboxylated at 150—160° to Et α -aceto- β -*p*-anisyl- Δ^{β} -butenoate, b.p. 189—191°/12 mm., which with 10% NaOH yields (V) and (VI).

(I) and 90% H_2SO_4 at room temp. for 4 hr. give, through an intermediate unstable acid, the isomeric lactonic acid (IX) (VIII with Et = H), m.p. 181°, converted by HCl into (III) and by NaOH into (II) and (VI); the Ag salt of (IX) and EtI give (VIII).

α -Aceto- β -2-methoxy-5-methylphenylglutaconic anhydride (X), m.p. 129° [prep. as for (I)], is converted by 20% HCl into β -2-methoxy-5-methylphenylpropylene (XI), b.p. 96—98°/12 mm., by 75% H_2SO_4 into the lactonic acid; m.p. 179° [structure as (IX)], and by *N*-NaOH into δ -keto- β -2-methoxy-5-methylphenyl- Δ^{α} -hexenoic acid, m.p. 101° (decomp.) (lactone, b.p. 212—214°/14 mm.), decarboxylated to δ -keto- β -2-methoxy-5-methylphenyl- Δ^{α} -pentene, b.p. 133°/4 mm. [semicarbazone, m.p. 169° (decomp.)], which with NaOBr gives 2-methoxy- β :5-dimethylcinnamic acid, m.p. 111°, in turn decarboxylated to (XI) and converted by warm conc. H_2SO_4 into 4:6-dimethylcoumarin. The α -Et₁ ester (semicarbazone, m.p. 158°), from (X) and EtOH, has m.p. 118° (decomp.). α -Aceto- β -4-methoxy-3-methylphenylglutaconic anhydride, m.p. 187° [corresponding α -Et₁ ester,

m.p. 126° (decomp.)], β -4-methoxy-3-methylphenylpropylene, b.p. 104—105°/6 mm., δ -keto- β -4-methoxy-3-methylphenyl- Δ^{α} -hexenoic acid, m.p. 139° (decomp.) [semicarbazone, m.p. 145° (decomp.)]; lactone, m.p. 91°, and δ -keto- β -4-methoxy-3-methylphenyl- Δ^{α} -pentene, b.p. 158°/4 mm., are described (cf. *loc. cit.*).

A. T. P.

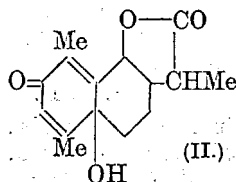
An anthelmintic santonin derivative. Y. ASAHINA and T. MOMOSE (Proc. Imp. Acad. Tokyo, 1938, 14, 112—114).—Hyposantonin [= deoxy-desmotroposantonin] (I) forms a 2- NO_2 -derivative, m.p. 183°, reduced in neutral solution to the 2- NH_2 -derivative, m.p. 193° (convertible by HNO_2 into 1-desmotroposantonin), which with Caro's acid gives the 2- NO -derivative, m.p. 146°, converted by Na_2SO_3 , through the hydroxylamine, into the OH-ketone (II), m.p. 222—223° (physiological properties discussed).

2-Hydroxylamino-5:6:7:8-tetrahydronaphthalene is similarly converted into 10-hydroxy-2-keto-2:5:6:7:8:10-hexahydronaphthalene, m.p. 124—125° (Ac derivative, m.p. 81°). A. T. P.

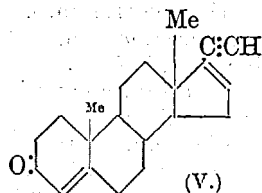
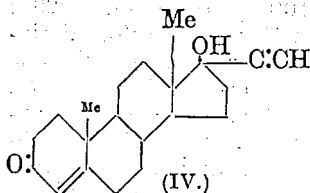
Saturated and unsaturated ketones of the pregnane series.—See B., 1938, 731.

Sterols and sexual hormones. XLIII. Preparation of 17-vinyltestosterone. L. RUZICKA, K. HOFMANN, and H. F. MELDAILL (Helv. Chim. Acta, 1938, 21, 597—601; cf. A., 1938, II, 276).—17-Vinyl- Δ^5 -androstene-3-*trans*-17-diol (I) (prep. from the $\text{C}:\text{CH}$ compound described), new m.p. 184—187°, $[\alpha]_D -64^\circ$ in abs. EtOH, is oxidised by $\text{Al}(\text{O}i\text{Bu})_3$ to 17-vinyltestosterone, m.p. 140—141°, $[\alpha]_D +87.6^\circ$ in abs. EtOH. The structure of (I) is proved by reduction by H_2 -Raney Ni to 17-ethylandrosterone-3-*trans*-17-diol, m.p. 200—202°, $[\alpha]_D -68.4^\circ$, oxidised by $\text{Al}(\text{O}i\text{Bu})_3$ to 17-ethyltestosterone. R. S. C.

Sex hormone series. H. H. INHOFFEN, W. LOGEMANN, W. HOHLWEG, and A. SERINI (Ber., 1938, 71, [B], 1024—1032; cf. A., 1938, II, 146).—Successive addition of C_2H_2 and oestrone to a solution of K in liquid NH_3 gives 17-ethinylœstra-3:17-diol (I), m.p. 145—146°, $[\alpha]_D +1^\circ$ in dioxan [benzoate, m.p. 200—202°, hydrolysed to (I)], which has about the same physiological activity as oestradiol (II) when given subcutaneously but is much more active when given orally. Similar results are recorded with 17-ethinyl-dihydro-equilin, m.p. 179°, and -equilenin, m.p. 179° (benzoate, m.p. 225°), obtained analogously. The high physiological activity is due to the presence of $\text{C}:\text{CH}$ since 17-vinylœstradiol (III), m.p. 148—150° after softening (clear at 157°), $[\alpha]_D +57.3^\circ$ in dioxan [benzoate, m.p. 160—162° after softening; clear at 164°], has activity similar to that of (II). Oxidation of (III) by OsO_4 in anhyd. Et_2O at room temp. gives 17- α,β -dihydroxyethylœstradiol, m.p. 207—208°; almost devoid of physiological activity. $\text{Al}(\text{OPr}^i)_3$ and (I) in boiling $\text{C}_6\text{H}_6\cdot\text{COMe}_2$ yield pregnenin-17-ol-3-one (IV) (ethinyltestosterone), m.p. 264—266°, $[\alpha]_D +21.5^\circ$ in dioxan [semicarbazone, m.p. 230—231° (decomp.)], which has about one third of the physiological activity of progesterone when given subcutaneously



but a much higher potency when administered *per os*. Reduction (Ni) of (IV) gives 17-vinylandrostene-3 : 17-



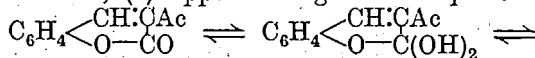
diol, m.p. 183—185°, $[\alpha]_D -71.4^\circ$ in dioxan, transformed by $\text{Al}(\text{OPr}^i)_3$ in boiling $\text{PhMe-cyclohexanone}$ into *pregnadien-17-ol-3-one*, m.p. 142°, $[\alpha]_D +77.6^\circ$ in dioxan [semicarbazone, m.p. 223° (decomp.)], which has about one fourth of the physiological activity of (IV). Boiling 90% HCO_2H transforms (IV) into the *anhydroketone* (V), m.p. 166°, which has no progesterone activity. H. W.

Water-soluble derivatives of sterols and steroids. A. ERCOLI and L. MAMOLI (Gazzetta, 1938, 68, 142—146).—Cholesterol and $\text{CHN}_2\text{CO}_2\text{Et}$ at 130—140° give a product hydrolysed (MeOH-KOH) to Δ^5 -cholesten-3-oxoacetic acid, m.p. 164.5—165°. Estrone similarly (or with $\text{CH}_2\text{Cl-CO}_2\text{H}$ in aq. KOH) gives 17-keto- α -estratrien-3-oxoacetic acid (I), m.p. 209° [*Me* ester (II), m.p. 226°]. Dehydroandrosterone likewise gives 17-keto- Δ^5 -androsen-3-oxoacetic acid (III), m.p. 203—205° [*Me* ester (IV), m.p. 137—138°]. The *Na* salts of (I) and (III), injected into castrated white mice, have activities of 75,000 and 1000 international units per g., respectively; (II) has a negative reaction in 10, positive in 50, and (IV) negative in doses of 1000 μg . when injected in oil. E. W. W.

Preparation of benzoylformaldehyde. S. CUSMANO (Gazzetta, 1938, 68, 129—131).—In H_2O . $\text{COPh}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ is converted by nitrous fumes into $\text{COPh}\cdot\text{CHO}$, with some 4 : 5-dibenzoyl-1 : 2 : 3 : 6-dioxadiazine (A., 1932, 1146). E. W. W.

Shift in configuration of certain α -benzilmonooxime benzoates. R. P. BARNES (J. Amer. Chem. Soc., 1938, 60, 1082—1083).— α - $\text{COPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{OR}$ [$\text{R} = \text{Bz}$, m.p. 85—86° (lit. 95—96°), p - $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}$, or p - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}$] (0.5—5 g.) gives the β -isomeride when heated with conc. HCl (10 drops) in EtOH (15—25 c.c.). Doubt is thus cast on much published evidence concerning the configuration of oximes. R. S. C.

Reaction of ω -halogenoketones with unsaturated compounds. Constitution of acetylcoumarin. S. BODFORSS (Annalen, 1938, 534, 226—243).—It appears improbable that the condensation of 3-acetylcoumarins with ω -halogenoketones in presence of alkali can occur with intermediate formation of *o*-quinones, e.g., o - $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CAc}\cdot\text{C}(\text{OH})\cdot\text{ONa}$ (Widman, A., 1918, i, 347, 393; 1919, i, 32, 55), since the mode of formation is very unusual for a keten and the intermediate does not tend to polymerise or to become oxidised by air. Further it is an acid of considerable strength and its absorption spectrum is nearly identical with that of o - $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$, thus suggesting that it is o - $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CAc}\cdot\text{CO}_2\text{H}$. The independence of the presence of a coumarin ring for the reaction is proved by the formation of 1-benzoyl-3-*p*-anisoyl-2-*o*-nitrophenylcyclopropane, m.p. 132°, from o - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$ (improved prep. from o - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and COPhMe in AcOH containing HCl and piperidine) and p - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ in $\text{COMe}_2\text{-EtOH-NaOEt}$, and of 1 : 2-dibenzoyl-3-*o*-nitrophenylcyclopropane, m.p. 177°, from $\text{COPh}\cdot\text{CH}_2\text{Cl}$. Negative results are obtained with $\text{CHPh}\cdot\text{CH}\cdot\text{COPh}$, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$, $\text{CO}(\text{CH}\cdot\text{CHPh})_2$, $\text{CO}(\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{-}m)_2$, dibenzoylstyrene, Et_2 *p*-nitrobenzylidenemalonate, o - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, benzoylcoumarone, and carvone. The possibility of the intermediate formation of a radical is rejected in favour of that of a halogenohydrin since in an analogous reaction $\alpha\beta$ -oxido- α -anisoyl- β -*o*-nitrophenylethane, m.p. 147°, and $\alpha\beta$ -oxido- α -benzoyl- β -anisylethane, m.p. 87°, are obtained from o - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and p - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ and from p - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and $\text{COPh}\cdot\text{CH}_2\text{Cl}$, respectively. The reaction thus appears analogous to the addition of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ or $\text{CH}_2(\text{CO}_2\text{Et})_2$ to double linkings. Attempts to condense these esters with 3-acetylcoumarin (I) do not give certain results by reason of secondary changes, but with $\text{CN}\cdot\text{CHPh}\cdot\text{NHPH}$ and piperidine a product, $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}$, m.p. 175°, is obtained whereby secondary changes appear to have occurred. In aq. solution, (I) appears to give the equilibria:



Widman's conception of the nature of the product of the action of alkali on (I) depends mainly on the yellow colour which develops in the solution, suggesting thus the presence of an *o*-quinone. Since it is now regarded as *Na* α -acetylcoumarate the absorption spectrum of this and of its possible parents PhOH , $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, $\text{COMe}\cdot\text{CH}\cdot\text{CHPh}$, and o - $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$ have been measured in acid and alkaline solution. The quinonoid structure is thereby disproved unless all phenols are to be regarded as quinones. H. W.

Steric hindrance in α -diketones. II. Mesitylbenzylglyoxal. R. P. BARNES (J. Amer. Chem. Soc., 1938, 60, 1168—1170; cf. A., 1935, 979).—Owing to steric hindrance 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{C}(\text{OH})\cdot\text{CHPh}$ reacts with MgPhBr solely by 1 : 4-addition to give the *Mg* compound, $\text{CHPh}_2\cdot\text{C}(\text{OMgBr})\cdot\text{C}(\text{OMgBr})\cdot\text{C}_6\text{H}_2\text{Me}_3$, which with BzCl yields $\alpha\beta$ -dibenzoyloxy- $\gamma\gamma$ -diphenyl- α -mesityl- Δ^{α} -propene, m.p. 158°, and is hydrolysed to an oil, b.p. 150—155°/2 mm., probably $\text{CHPh}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$, which is readily enolised by hot NaOH-MeOH to β -hydroxy- $\alpha\alpha$ -diphenyl- γ -mesityl- Δ^{α} -propen- γ -one [mesitylbenzylglyoxal] (I), m.p. 120° (red FeCl_3 colour; gives no oxide with H_2O_2). The structure of (I) is proved by synthesis from $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ by way of the oxide. (I) is completely enolised, giving 1 mol. of CH_4 with MgMeI . It gives a $\text{Cu}_{0.5}$, m.p. 123° (decomp.), and *Na* derivative. With Br in Et_2O it gives HBr and α -bromo- $\alpha\alpha$ -diphenyl- γ -mesitylpropane- $\beta\gamma$ -dione (II), m.p. 155°, reduced to (I) by HI . KMnO_4 oxidises (I) partly to COPh_2 and $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$ and partly to $\gamma\gamma\delta\delta$ -tetraphenyl- $\alpha\alpha$ -dimesitylhexane- $\alpha\beta\epsilon\zeta$ -tetraone, m.p. 192°, also obtained

from the Na derivative of (I) by I in Et₂O. The $\text{>C}\cdot\text{C}\cdot\text{<}$ linking is rather weak, since H₂O₂ slowly oxidises the substance to C₆H₅CO₂H and Br-CHCl₃ converts it into (II). With NaOMe-MeI (I) gives the β -OMe-compound, m.p. 53°. With KOAc in hot AcOH (II) gives α -acetoxy- α -diphenyl- γ -mesitylpropane- β - γ -dione, m.p. 132°, hydrolysed during isolation to α -hydroxy- α -diphenyl- γ -mesitylpropane- β - γ -dione, m.p. 125°, and obtained therefrom by AcCl. HBr-AcOH regenerates (II) from the OH-compound.

R. S. C.

Indene derivatives from aromatic ketocarboxylic esters. G. WOJACK (Ber., 1938, 71, [B], 1102—1116; cf. A., 1937, II, 457).—COPh·CHEt·CO₂Et (reacting as OH·CPh·CET·CO₂Et) is converted by conc. H₂SO₄ at 100° into 2-ethylindane-1:3-dione, m.p. 55.5°; the unstable 2-P^r, m.p. 50.5°, and -Bu^a, m.p. 33°, derivatives are obtained similarly. *p*-NO₂·C₆H₄·CH₂·CHBz·CO₂Et gives 2-*p*-nitrobenzylindane-1:3-dione, m.p. 143°, converted by NaOEt and CH₂PhCl in boiling EtOH into 2-benzyl-2-*p*-nitrobenzylindane-1:3-dione, m.p. 141°, also obtained from 2-benzylindane-1:3-dione and *p*-NO₂·C₆H₄·CH₂Cl. Et 1-naphthoyletacetate and conc. H₂SO₄ at 80° give a product (A), m.p. 245—252° (decomp.), yellow leaflets or needles, which contains H₂SO₄ but does not appear to have an ester or oxonium salt structure. From its cold solutions benzidine or BaCl₂ in EtOH or AcOH ppts. the corresponding sulphate whilst BaCO₃ removes H₂SO₄ from the solution in EtOH with crystallisation of perinaphthindanedione; the solubility of the latter in H₂O, EtOH, or AcOH is greatly increased by the presence of mineral acid but it does not appear possible to obtain (A) from it and 96% H₂SO₄. Et 2-naphthoyletacetate is smoothly converted by conc. H₂SO₄ into 4:5-benzointhane-1:3-dione. Et α -1-naphthoyletpropionate (I) and conc. H₂SO₄ at 110° give a mixture of 2-methyl-4:5-benzointhane-1:3-dione (II), m.p. 110° (whence 2:2-dimethyl-4:5-benzointhanedione, m.p. 121°), and 2-methylperinaphthindanedione, m.p. 176—177° (decomp.) (also +1 HCO₂H, m.p. 173° after softening at about 100°). (II) is also obtained from Et α -2-naphthoyletpropionate and conc. H₂SO₄ or POCl₃ containing a definite proportion of HCl and H₃PO₄. PCl₅ in boiling CCl₄ transforms (II) into 1:1:3:3-tetrachloro-2-methyl-4:5-benzointhane, m.p. 103°, whilst under similar conditions (I) gives 1:1:2:3:3-pentachloro-2-methyl-4:5-benzointhane, m.p. 145.5°. This with 96% H₂SO₄ at 100° affords 2-chloro-2-methyl-4:5-benzointhane-1:3-dione, m.p. 132°, also derived from (II) and SO₂Cl₂. The following compounds are obtained by similar methods: 2-ethyl-4:5-benzointhane-1:3-dione, m.p. 116°, whence the 2:2-Et₂ compound, m.p. 97°; 2-ethylperinaphthindanedione, m.p. about 186° (decomp.) [also (?) +1 HCO₂H]; 2-*n*-propyl-4:5-benzointhane-1:3-dione, m.p. 69°; (?) 2-*n*-propylperinaphthindanedione, decomp. about 220°; 2-benzyl-, m.p. 129°, 2-*p*-nitrobenzyl-, m.p. 186°, and 2-*p*-phenylbenzyl-, m.p. 136°, -4:5-benzointhane-1:3-dione. H. W.

trans-2:3-Diketodecahydronaphthalene. K. GANAPATHI (Current Sci., 1938, 6, 448—449; cf. Wallach and Weissenborn, A., 1924, i, 862).—*trans*- β -

Ketodecahydronaphthalene (I) is oxidised (SeO₂ in boiling EtOH) to *trans*-2:3-diketodecahydronaphthalene (II), m.p. 99—100° (dioxime, m.p. 229°; disemicarbazone, m.p. 264—265°; quinoxaline derivative, m.p. 177—178°), which differs from the diketone described by Rao and Kuppaswamy (A., 1938, II, 15). (II) is oxidised by H₂O₂ to *trans*-cyclohexane-1:2-diacetic acid, is reduced by Na-Hg to *trans*-2:3-dihydroxydecahydronaphthalene, and is converted by NaOH into *trans*-2-hydroxyhexahydroindene-2-carboxylic acid. HNO₃ oxidises (I) to cyclohexane-1:2-diacetic acid, together with a little of the 1-carboxy-2-propionic acid. A. LI.

Biochemistry of micro-organisms. LVIII. Synthesis of spinulosin (3:6-dihydroxy-4-methoxy-2:5-toluquinone), metabolic product of *Penicillium spinulosum*, Thom. W. K. ANSLOW and H. RAISTRICK (Biochem. J., 1938, 32, 803—806).—6-Hydroxy-4-methoxy-2:5-toluquinone (prep. described) and aq. EtOH-NH₂Me (12—14 mols.) give 3:6-di(methylamino)-4-methoxy-2:5-toluquinone, m.p. 215°, hydrolysed (10N-H₂SO₄) to spinulosin (cf. A., 1938, III, 443), which is reduced (Na₂S₂O₄) to 3:6-dihydroxy-4-methoxytoluquinol, m.p. 167° (yellow colour with conc. H₂SO₄, changing to emerald-green and finally plum colour; greenish-black colour with EtOH-FeCl₃). P. G. M.

Constitution and reactivity. XX. Kinetics of the nitration of 1-nitroanthraquinone. K. LAUER, R. ODA, and K. TAMURA (J. pr. Chem., 1938, [ii], 151, 45—48; cf. A., 1937, II, 331).—*k* for the nitration of 1-nitroanthraquinone by 1 mol. of KNO₃ in 93, 98, and 100% H₂SO₄ is determined at 25—50°. It decreases as the concn. of the acid increases and depends on the activation energy, which similarly decreases. The val. found for *k* agrees with that calc. for 100% H₂SO₄, but for 93 and 98% acid is 16,000 and 15,000, respectively, times too large.

R. S. C.

New structural isomeride of campholic acid; β -campholic acid. F. SALMON-LEGAGNEUR (Compt. rend., 1938, 206, 1021—1023; cf. A., 1932, 1037).—The semicarbazone of Et camphoceanaldehyde with K at 200—300° affords β -campholic acid [2:2:3:3-tetramethylcyclopentane-1-carboxylic acid], m.p. 65—66.5° (Me, b.p. 96—97°/15 mm., and Et, b.p. 115—116°/20 mm., esters; amide, m.p. 124—125°, and the corresponding nitrile, m.p. 119—120°). The crude acid prepared from *d*-camphor is weakly *d*-rotatory, but after recrystallisation it is inactive, as are its derivatives. This synthesis indicates that isocampholic acid cannot have the structure suggested by Blanc (cf. A., 1922, i, 735). J. L. D.

Camphor from Italian colonies. A. BORIANI (Ann. Chim. Farm., 1039, 1, 47—52).—Camphor from *Merianda* plants grown in Eritrea has m.p. 171° (or lower), and [α]_D²⁰ +7.2° in EtOH. E. W. W.

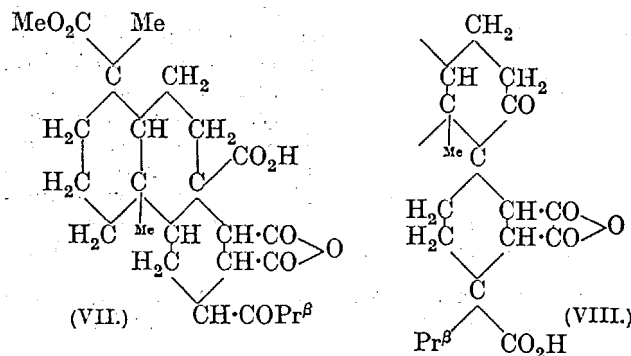
New method of resolving a racemic compound. G. M. HENDERSON and H. G. RULE (Nature, 1938, 141, 917—918).—A partial resolution of inactive *p*-phenylenebisiminocamphor has been effected by allowing a dil. solution in petroleum + C₆H₆ to flow down a tube packed with lactose, and washing the

broad yellow adsorbed band with the solvent until it fills the tube. The *d*- is more strongly adsorbed than the *l*-isomeride on lactose. L. S. T.

Diterpenes. XXXIV. Formation and degradation of tetrahydroxyabiatic acid. L. RUZICKA and L. STERNBACH [with, in part, R. LUKES, F. ZWICKY, and R. G. R. BACON]. **XXXV. Oxidative degradation of *l*-pimaric acid and of its additive product with maleic anhydride.** L. RUZICKA, R. G. R. BACON, R. LUKES, and J. D. ROSE. **XXXVI. So-called pyroabiatic acid.** L. RUZICKA, R. G. R. BACON, L. STERNBACH, and H. WALDMANN (Helv. Chim. Acta, 1938, 21, 565—583, 583—591, 591—597; cf. A., 1938, II, 195).—**XXXIV.** The position of the ethylenic linkings in abiatic acid (I) cannot be decided by absorption spectra or known facts. Steele's (I) and KMnO_4 at 0° give dihydroxyabiatic acid (II), $\text{C}_{20}\text{H}_{34}\text{O}_4$, m.p. $153\text{--}154^\circ$, $[\alpha]_D^{20} -29.7^\circ$ in EtOH [absorbs 1 O from BzO_2H ; resists $\text{H}_2\text{-PtO}_2$; faint colour with $\text{C}(\text{NO}_2)_4$], and an unstable compound, which with warm, dil. H_2SO_4 gives tetrahydroxyabiatic acid (III), m.p. $248\text{--}250^\circ$ (*Me* ester, m.p. $221\text{--}222.5^\circ$), but with dil. HCl gives *chlorotrihydroxyabiatic acid* (IV), $\text{C}_{20}\text{H}_{33}\text{O}_5\text{Cl}$, m.p. $148\text{--}149^\circ$ (decomp.) (*Me* ester, m.p. $156\text{--}158^\circ$). With cold, dil. H_2SO_4 the unstable compound gives a mixture, m.p. $220\text{--}225^\circ$, which reacts with HCl-COMe_2 and probably contains about 33% of an isomeric precursor of (IV). With warm NaOH (IV) loses HCl to yield a saturated oxido-compound, $\text{C}_{20}\text{H}_{32}\text{O}_5$, m.p. $126\text{--}130^\circ$, which regenerates (IV) with HCl and gives (III) with dil. H_2SO_4 . With $\text{Ac}_2\text{O-NaOAc}$ (III) loses H_2O and gives a *diacetate*, $\text{C}_{24}\text{H}_{36}\text{O}_7$, m.p. 233° (*Me* ester, m.p. 218°), which regenerates (III) when hydrolysed by NaOH. With $\text{Pb}(\text{OAc})_4$ (III) gives an indefinite substance (V), $\text{C}_{20}\text{H}_{30}\text{O}_6$ or $\text{C}_{20}\text{H}_{28}\text{O}_5$ [disemicarbazone, m.p. about $170\text{--}180^\circ$ (decomp.)], and an isomeric *tetrahydroxyabiatic acid*, m.p. $207.5\text{--}209^\circ$; with NaOBr (V) yields a tetracarboxylic acid (VI), $\text{C}_{15}\text{H}_{22}\text{O}_8$, m.p.

*Me*₃ (prep. by hot HCl-MeOH), m.p. $104\text{--}106^\circ$, and *Me*₄ ester (prep. by CH_2N_2), m.p. $73.5\text{--}74.5^\circ$ (no semicarbazone)]. (I) is thus possibly (Ia) or (Ib), which would yield respectively (Va) [or (Vc)] and (Vb), and thence (VI). The consequences of the inactivity of the acids, $\text{C}_{12}\text{H}_{18}\text{O}_6$ and $\text{C}_{11}\text{H}_{16}\text{O}_6$ (cf. A., 1931, 736) are discussed.

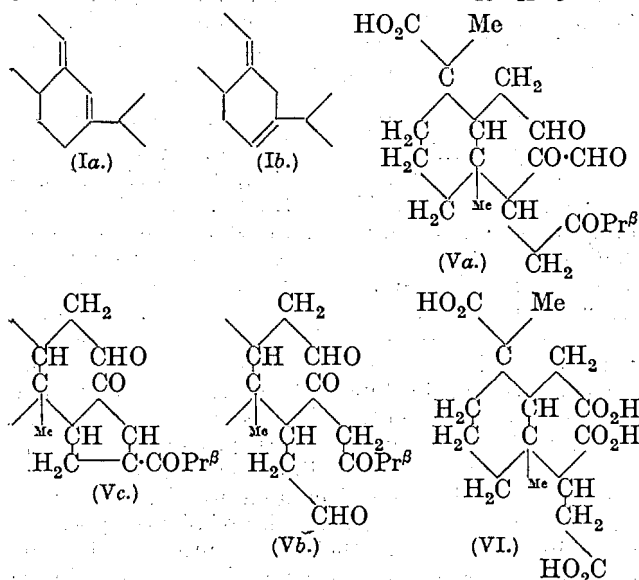
XXXV. The $(\text{CH-CO})_2\text{O}$ adduct of *Me* abiatic acid with O_3 in AcOH-EtOH gives a *Me* ester (VII) or (VIII), $\text{C}_{25}\text{H}_{34}\text{O}_8$, m.p. about 265° (rapid heating) or $248\text{--}250^\circ$ (decomp.; slow heating) [with $\text{NH}_2\text{-NH-CO-NH}_2$ gives a product (9.6% N), m.p. about $240\text{--}245^\circ$ (decomp.)]; CH_2N_2 gives an amorphous (?) *Me*₄ ester], Clemmensen reduction of which gives a 2%



yield of a saturated substance, $\text{C}_{24}\text{H}_{34}\text{O}_7$, m.p. 295° (*Me* ester, m.p. 200°). This or the crude reduction product is dehydrogenated by Pd-C at 330° to an oily hydrocarbon, $\text{C}_{19}\text{H}_{20}$ [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ additive compound, m.p. 138°], not identical with 1-methyl-6-isobutylphenanthrene, m.p. $49\text{--}50^\circ$ [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ additive compound, m.p. $134\text{--}135^\circ$; quinone, m.p. $157\text{--}159^\circ$; expected from (VII)]. *l*-Pimaric acid with KMnO_4 (2 O) gives an indefinite mixture of (?) $(\text{OH})_2$ -acids, with more KMnO_4 (4 O) gives an acid, $\text{C}_{20}\text{H}_{32}\text{O}_5$ and with O_3 in CCl_4 gives $\text{Pr}^{\beta}\text{CO}_2\text{H}$.

XXXVI. Fractionation of pyroabiatic acid gives *dihydroabiatic acid*, m.p. $193\text{--}194^\circ$, $[\alpha]_D +9^\circ$ in EtOH (hydrogenated to a *H*₄-acid, m.p. 180°), and an acid, $\text{C}_{20}\text{H}_{30}\text{O}_2$, m.p. $168\text{--}169^\circ$, $[\alpha]_D +53^\circ$ in EtOH or CHCl_3 (absorbs 4 H catalytically; possibly = Fieser's pyroabiatic acid). Fractional adsorption of the crude *Me* ester yields the *Me* ester, m.p. $62\text{--}62.5^\circ$, of *dehydroabiatic acid*, m.p. about $172\text{--}174^\circ$ after sintering at 160° , $[\alpha]_D +64^\circ$ in EtOH, $+76^\circ$ in C_6H_6 . Absorption max. are detailed. All m.p. above are corr. R. S. C.

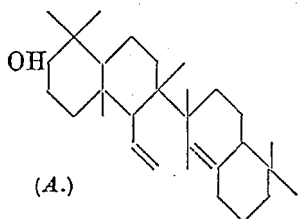
Triterpene group. I. β -Boswellic acid. J. C. E. SIMPSON and N. E. WILLIAMS (J.C.S., 1938, 686—688).—*Me* β -boswellate, m.p. $195\text{--}195.5^\circ$, $[\alpha]_D^{25} +161^\circ$ in CHCl_3 , is oxidised ($\text{CrO}_3\text{-AcOH}$) to a *keto-ester*, $\text{C}_{31}\text{H}_{48}\text{O}_3$, m.p. $159\text{--}160^\circ$ (*oxime*, m.p. 210°). Oxidation of β -boswellic acid (I) gives *nor- β -boswellone*, m.p. $195\text{--}196^\circ$ (*oxime*, m.p. $164\text{--}167^\circ$), reduced (Zn-AcOH) to a hydrocarbon, $\text{C}_{29}\text{H}_{48}$, m.p. $168\text{--}169^\circ$, $[\alpha]_D^{25} +143^\circ$ in CHCl_3 ; the ketone is further oxidised (KMnO_4) to a *ketone*, $\text{C}_{26}\text{H}_{42}\text{O}_2$, m.p. $217\text{--}218^\circ$, $[\alpha]_D^{25} +157^\circ$ in CHCl_3 (*semicarbazone*, m.p. $238\text{--}239^\circ$; *product*, m.p. $197\text{--}198^\circ$, with $\text{NH}_2\text{OH, AcOH}$). These reactions indicate that (I)



$245\text{--}246.5^\circ$ (rapid heating), $[\alpha]_D^{20}$ about -6° in EtOH [*Me*₂ (prep. by cold HCl-MeOH), m.p. $160\text{--}160.5^\circ$,

is a β - and not an α -OH-acid (cf. Trost, A., 1937, II, 382). F. R. S.

Lupeol. III. H. DIETERLE and F. BIEDEBACH [with, in part, O. WIEGAND] (Arch. Pharm., 1938, 276, 312—315; cf. A., 1933, 162).—Oxidation (CrO_3 in AcOH at 100°) of lupeol acetate (I), conversion of the mixture of acids thus produced into their Na salts which are treated with CH_2N_2 , and further oxidation of the product leads to the Me ester, $\text{C}_{30}\text{H}_{48}\text{O}_3$, m.p. 263° (2:4-dinitrophenylhydrazone, m.p. 181°), of a CO-acid. It is thus probable that lupeol (II) contains the vinyl group; this view is strengthened by the isolation of CH_2O and HCO_2H



by the ozonolysis of (I). Titration of (I) and (II) with BzO_2H in CHCl_3 gives the corresponding dioxides, m.p. 228° and 189° , respectively, whereas lupeylene gives a non-cryst. trioxide. (I) and (II) therefore contain a second double link-
ing which cannot be hydrogenated. The skeleton of (II) is possibly (A). H. W.

Preparation, properties, and mode of occurrence of laminarin.—See A., 1938, III, 631.

Quassin. III. **Picrasmin.** E. P. CLARK (J. Amer. Chem. Soc., 1938, 60, 1146—1148; cf. A., 1938, II, 66).—**Picrasmin**, $\text{C}_{22}\text{H}_{30}\text{O}_6$, m.p. 218° , $[\alpha]_D^{25} +45.4^\circ$ in CHCl_3 , is obtained in 0.1% yield from the wood of *Picrasma excelsa* and resembles quassin in being converted by 3.5% HCl into semidemethoxyquassin, by HCl - AcOH into quassinol (but in 33% better yield), by CrO_3 - AcOH into isoquassin, and by hot, dil. KOH - EtOH into indefinite material. It is unaffected by HCl - EtOH and with Ac_2O - NaOAc gives only dehydroquassin. The structures must thus be very similar. R. S. C.

Constitution of clerodin. H. N. BANERJEE (Trans. Bose Res. Inst., 1935—1936, 11, 71—81).—**Clerodin** (A., 1937, II, 287), $\text{OH}\cdot\text{C}_{11}\text{H}_{14}\cdot\text{OAc}$, has m.p. 162° and $[\alpha]_D -47.6^\circ$ in CHCl_3 . It gives a Bz, b.p. $140^\circ/1\text{ mm.}$, and Ac derivative, m.p. 110° , phenylurethane, m.p. 240° (decomp.), dibromide (prep. in CHCl_3), m.p. 170° (decomp.), and Br-derivative [dibromide, m.p. 110° (decomp.)]. It is mono-unsaturated to Br and I, with HI gives a $(\text{OH})_2$ -compound, m.p. 250° (converted into clerodin by Ac_2O), and gives a pink colour (sol. in $\text{C}_5\text{H}_{11}\cdot\text{OH}$; absorption max. 4690 — 5070 \AA.) with NH_3 in AcOH . It is anthelmintic *in vitro*. The sterol from *Clerodendron infortunatum* has $[\alpha]_D -25.6^\circ$ in CHCl_3 and I val. 124.5 and is thus doubly unsaturated.

R. S. C.

Ketone formation in the sulphonation of heat-treated rosin. T. HASSELSTROM, E. A. BRENNAN, and J. D. MCPHERSON (J. Amer. Chem. Soc., 1938, 60, 1267).—Heat-treated rosin or ψ -pimaric acid with conc. H_2SO_4 at about 0° gives a sulphonic acid, m.p. 222 — 223° (decomp.), and the lactone, m.p. 130 — 131° , of Ruzicka *et al.* (A., 1922, i, 547; 1933, 280).

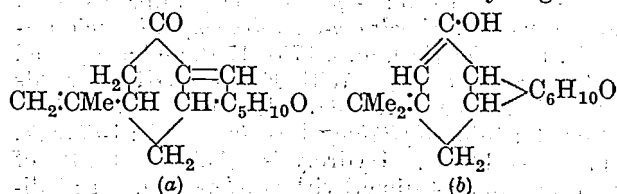
R. S. C.

Resins. III. **Oxidation of the laevorotatory primary pine resin acid (*l*-pimaric acid).** H. WIENHAUS and W. SANDERMANN (Ber., 1938, 71, [B], 1094—1102).—Oxidation of K *l*-pimarate by KMnO_4 in H_2O and treatment of the solution with CO_2 gives small amounts of an acid, m.p. 172° , $[\alpha]_D -61.2^\circ$ in Et_2O , whilst AcOH gives a mixture (I) of amorphous acids from which minute amounts of a dihydroxy-resin acid, $\text{C}_{20}\text{H}_{30}\text{O}_2(\text{OH})_2$, m.p. 243° , separate. CH_2N_2 and (I) afford Me 1-oxidodihydroxy-pimarate (II), $\text{C}_{21}\text{H}_{34}\text{O}_5$, b.p. 300° (bath)/ 12 mm. , m.p. 183° (corr.), which is unusually stable towards KOH , and contains 2 OH (Tschugaev-Zerevitinov) and a γ - or δ -oxide ring. It appears saturated towards $\text{C}(\text{NO}_2)_4$ in Et_2O , catalytic hydrogenation, and the limited action of O_3 . With HCl in dry Et_2O at 0° it yields the substance, $\text{C}_{21}\text{H}_{33}\text{O}_4\text{Cl}$, m.p. 167° , thus indicating the presence of *tert.* OH, whilst under more drastic conditions the compound, $\text{C}_{21}\text{H}_{33}\text{O}_3\text{Cl}$, m.p. 145 — 147° , results. The ready formation of a cryst. monoacetate, m.p. 124° , points to a *sec.* or primary OH. The *cis* position of the 2 OH to one another follows from the observation that neutralised $\text{Na}_2\text{B}_4\text{O}_7$ becomes acid to phenolphthalein on addition of the ester. (II) is little affected by KMnO_4 and is transformed by $\text{Pb}(\text{OAc})_4$ into a viscous yellow mass. It is oxidised by HNO_3 to a monocarboxylic acid, (?) $\text{C}_{21}\text{H}_{30}\text{O}_8$, m.p. about 243° (decomp.), and by CrO_3 ($\approx 2-3\text{ O}$) at room temp. to an amorphous product which when heated with COMe_2 yields platelets (III), m.p. 169° , and with MeOH gives more sparingly sol. coarse crystals (IV), m.p. 221° . (III) is also produced in small amount when only so much CrO_3 is used as is necessary to transform $\text{CH}\cdot\text{OH}$ into CO . These isomeric substances $\text{C}_{21}\text{H}_{32}\text{O}_6$ are neutral, contain 1 OH (Tschugaev-Zerevitinov), and react with warm KOH - EtOH in the ratio 1:1. Since the ester group is hydrolysed with much greater difficulty the fission of a lactone group is assumed. (IV) is further degraded by CrO_3 to a compound, $\text{C}_{18}\text{H}_{26}\text{O}_5$, m.p. 136° (oxime, m.p. 180°), which contains 1 OH. Its oxidation with KMnO_4 leads to a monocarboxylic acid, $\text{C}_{17}\text{H}_{28}$ (or 26) O_8 , m.p. 139° (K salt). H. W.

Degradation of different species of wood and straw by alkali and copper oxide-ammonia. R. S. HILPERT and W. HANSI (Ber., 1938, 71, [B], 933—937; cf. A., 1937, II, 110, 204, 205).—The behaviour of cypress, red beech, alder, and straw towards conc. NaOH alone and in the presence of CS_2 at room temp. and of the alkali-sol. and insol. products towards Schweitzer's solution has been examined. Products of the composition $\text{C}_6\text{H}_{10}\text{O}_5$ are scarcely observed. Only from red beech had one reaction produced approx. the composition of cellulose (I) but it failed to dissolve in Schweitzer's reagent. There is no reason to assume that (I) with its typical chemical properties occurs in woods. Great chemical differences exist between the woods of the pine, deciduous woods, and straw. The cell walls of different species of plants appear to differ in the details of their constitution so that the components or reaction products known as cellulose and hemicelluloses may have great differences among themselves. II. W.

Lichen substances. LXXXVIII. Zeorin group. I. Y. ASAHINA and H. AKAGI (Ber., 1938, 71, [B], 980—985).—Extraction of the thalli of *Parmelia leucotylica*, Nyl., with Et₂O affords atranorin and a mixture of neutral substances separated chromatographically (Al₂O₃) into zeorin (I), C₃₀H₅₂O₂, m.p. 253°, [α]_D²⁵ +101.4° in C₅H₅N, and *leucotylin* (II), C₃₀H₅₂O₃, m.p. 333°, [α]_D²⁵ +49.43° in C₆H₅N. Ac₂O in C₅H₅N at 100° converts (I) into a *monoacetate*, m.p. 178°, which does not give a colour with C(NO₂)₄ in CHCl₃, whereas boiling Ac₂O transforms it into *anhydrozeorin acetate*, m.p. 158°, which gives a yellow colour with C(NO₂)₄ and is hydrolysed by KOH-MeOH to *anhydrozeorin*, m.p. 203°. Agathalin (III) is obtained when (I) and Se are heated at 340—350°. All the O atoms of (II) are present as alcoholic OH, one of which is *tert.* since (II) is transformed by Ac₂O in C₅H₅N into the *diacetate*, m.p. 240°, but by boiling Ac₂O into *anhydroleucotylin diacetate* (IV), m.p. 178°, hydrolysed to *anhydroleucotylin*, m.p. 235°. Hydrogenation (Pd sponge in AcOH) of (IV) yields *deoxyzeorin diacetate*, m.p. 95—105° (probably a mixture of isomerides), whence *deoxyzeorin*, m.p. 272—273°, [α]_D²⁵ +66.41° in C₅H₅N. Degradation of (II) by Se gives (III), so that very probably (II) is hydroxyzeorin. The production of (III) from betulin and agathendicarboxylic acid is recorded. H. W.

Constitutions of eremophilone, hydroxyeremophilone, and hydroxydihydroeremophilone. II. A. E. BRADFIELD, N. HELLSTRÖM, A. R. PENFOLD, and J. L. SIMONSEN (J.C.S., 1938, 767—774).—A more convenient method of separation of eremophilone (I) and hydroxyeremophilone (II) has been devised and from the mixture a ketone, C₁₅H₂₂O (2:4-dinitrophenylhydrazine, m.p. 155—156.5°), has been obtained. Catalytic hydrogenation of hydroxyeremophilone benzoate (III) gives a product which is not homogeneous (cf. A., 1933, 71), and from which β-hydroxydihydroeremophilone, m.p. 89—90°, [α]_D²⁵ +42° in MeOH, has been isolated, together with (by oxidation with H₂O₂) a *phenol*, C₁₅H₂₂O₃, m.p. 136—137°, and an *acid*, C₁₅H₂₄O₄, m.p. 193—195°. Oxidation of (II) with H₂CrO₄ gives a *phenol*, C₁₂H₁₈O₃, m.p. 193—194.5° (*Ac* derivative, m.p. 164—165°; *Me* ether, m.p. 121—122°), also obtained by ozonolysis of (II) together with a *keto-acid*, C₁₀H₁₆O₃, m.p. 105—107°, [α]_D²⁵ +28.27° in MeOH (*semicarbazone*, decomp. 215—216°). Ozonolysis of the *Me* ether, b.p. 180°/13 mm., of (II) yields the *keto-acid*, which is reduced (Zn-HCl) to an acid (p-phenylphenacyl ester, m.p. 65—67°, [α]_D²⁵ +15.3° in EtOAc), not identical with 2:2-dimethylcyclohexylacetic acid. Prolonged ozonolysis of (III) affords the *keto-acid* together with a *moloxide* of BzOH, C₇H₆O₄, decomp. 230—232°, whilst shorter time of ozonolysis gives an



oxide, C₁₉H₂₀O₅, m.p. 186—188°. Alternative formulae for (I) and (II) are discussed; the skeletons (a)

and (b) respectively being suggested, but a final decision must await further experiment. F. R. S.

Mango "chep," the exudation of the fruit of *Mangifera indica*. S. K. VASISTHA and S. SIDDIQUI (J. Indian Chem. Soc., 1938, 15, 110—117).—Dry mango "chep" contains a resin, *mangiferen*, C₂₁H₃₄O, (I), m.p. 63—65°, b.p. 308—310°/5 mm., [α]_D²⁵ +60° in EtOH, *mangiferic acid*, C₄₀H₆₀O₄ (II), m.p. 68—70°, [α]_D²⁵ +32° in EtOH [*Ac*₂ derivative (?), decomp. ~230°], and a phenol, *mangiferol*, (C₂₁H₃₆O₂)₅ (*Pb* salt). (I) is stable to KOH at 220°, and to conc. H₂SO₄ or HNO₃; with KMnO₄-COMe₂ it gives *oxymangiferen*, C₂₁H₃₄O₂, and on dry distillation two substances, C₁₅H₂₆ and C₁₅H₂₄. With fuming HNO₃ it yields a *dicarboxylic acid* (?), C₈H₁₂O₄; (I) and (II) absorb 2 Br and 4 Br, respectively, per mol. Fresh mango "chep" gives similar products; the odorous principle is not isolated by steam-distillation. E. W. W.

Poison of an Argentine toad. V. DEULOFEU and J. R. MENDIVE (Annalen, 1938, 534, 288—292).—The poison of an Argentine toad, probably *Bufo paracnemis*, is shown to contain marinobufogin, marinobufotoxin, bufotenin (I), and adrenaline (II). The toxin of the tropical *B. marinus* is mainly composed of (I) and (II). The presence of dehydrobufotenin, bufothionin, and other basic components could not be detected. H. W.

Analogues of ascorbic acid containing six-membered rings. W. N. HAWORTH, E. L. HIRST, and J. K. N. JONES (J.C.S., 1938, 710—715).—The additive product of 3-methylglucosone with HCN does not rearrange to form a substance analogous to ascorbic acid (I). The oxidation products (HNO₃) from 1:3:4:6-tetramethylfructose with MeOH-NaOMe give *Me* 3-hydroxy-4-methoxy-α-pyrone-6-carboxylate, m.p. 207° [which with CH₂N₂ affords the 3:4-(OMe)₂-compound, m.p. 93°]; and 3-hydroxy-4-methoxy-6-methoxymethyl-α-pyrone (II), m.p. 88° [3:4-(OMe)₂-compound, b.p. 135°/0.02 mm.]. These α-pyrone derivatives may be regarded as analogues of (I) containing 6-membered rings and they have properties similar to 3-methylascorbic acid and absorption spectra generally resembling those of members of the ascorbic acid series but with the heads of the bands situated at somewhat longer λ. The product, C₈H₁₀O₅, m.p. 89°, formed as one of the oxidation products of tetramethylfructofuranose is identical with (II). Et₂C₂O₄ and Et succinate (NaOEt) condense to form 3-hydroxy-α-pyrone-6-carboxylic acid and αα'-diketoadipic acid, m.p. 227° (*Me*₄ derivative, m.p. 116°); the pyrone-acid with CH₂N₂ affords *Me* 3-methoxy-α-pyrone-6-carboxylate, m.p. 215°. F. R. S.

Effect of the nature of the ring on the physical properties of some isomeric 1:4- and 1:5-epoxides. R. PAUL (Compt. rend., 1938, 206, 1028—1030).—2-Bromotetrahydropyran with MgRBr affords 2-alkyl or -aryl derivatives (I). The following are prepared: 2-methyl-, b.p. 101—103°/758 mm., -ethyl-, b.p. 128—129°/773 mm., -propyl-, b.p. 153—154°/768 mm., -butyl-, b.p. 64°/14 mm., and -phenyl-tetrahydropyran, b.p. 111—112°/10 mm. 2-Alkyl or -alkylene-furans when reduced afford 2-alkyltetra-

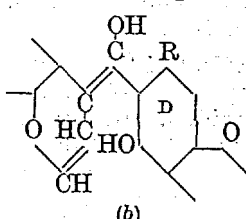
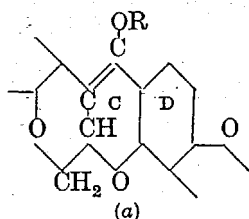
hydrofurans (II). The following are prepared: 2-methyl-, b.p. 108°/758 mm., -ethyl-, b.p. 135°/773 mm., -propyl-, b.p. 159—160°/768 mm., -butyl-, b.p. 70—71°/14 mm., and -phenyl-tetrahydrofuran, b.p. 109—110°/10 mm. Other physical properties of the above compounds are also listed. The 6-ring derivatives have b.p. 6—7° < the 5-ring containing the same substituent but η is about 10% greater. The mol. vol. and parachor of (I) are < those of the structurally isomeric (II). The differences are connected with the stereochemical differences in the rings (cf. A., 1932, 1190). J. L. D.

2:4-Diketo-6-methyl-3:3-diallyl- and -di-n-propyl-dihydropyran.—See B., 1938, 627.

α -Tocopherol. P. KARRER, H. FRITZSCHE, B. H. RINGIER, and H. SALOMON (Helv. Chim. Acta, 1938, 21, 520—525).—5-Hydroxy-2-methylcoumaran (*allophanate*, m.p. from 189°) resembles α -tocopherol (I) in absorption spectrum. Trimethylquinol, phetyl bromide, and ZnCl_2 in C_6H_6 at 60—70° give dl- α -tocopherol, an oil, the nitrophenylurethane, m.p. 131°, *allophanate*, m.p. 172°, and 2:4-dinitrobenzoate, m.p. 63°, of which do not depress the m.p. of the respective derivatives of (I) and which shows vitamin-E activity. The formation of Fernholz's γ -lactone (A., 1938, II, 186) is not evidence of a chroman as against a coumaran structure, since many β -OH-acids give γ -lactones. R. S. C.

Chroman structure of α -tocopherol. W. JOHN, E. DIETZEL, P. GÜNTHER, and W. EMTE (Naturwiss., 1938, 26, 366—367).—The spectrum of synthetic dl- α -tocopherol (I) of Karrer *et al.* (preceding abstract) is similar to that of a chroman rather than a coumaran derivative. Oxidation of (I) with AgNO_3 followed by reductive esterification with $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{COCl}$ gives a di-*p*-bromobenzoate, m.p. 115°, stable towards CrO_3 . The OH and consequently the arrangement of the ether ring is therefore *tert.* as required by a coumaran formulation. H. W.

Methylation and ease of ring-fission of rotenone and related substances. R. S. CAHN, R. F. PHIPERS, and J. J. BOAM (J.C.S., 1938, 734—741).—Substances of the rotenone and toxicarol series are methylated by Me_2SO_4 in boiling COMe_2 in the presence of either aq. KOH or anhyd. K_2CO_3 (containing 1% H_2O). Rotenone (I), deguelin (II), and similar substances give Me ethers derived from the enolic form (a), whilst toxicarol (III) and dihydrotoxicarol, which contain phenolic OH, give ethers derived from the "open" form (b). This difference shows the greater ease of fission of ring c induced by the phenolic



OH in D and confirms the views expressed previously (cf. A., 1938, II, 242). The two types of ether differ markedly in stability to acids, alkalis, and oxidising

agents, and in absorption spectra. (I) and Me_2SO_4 give mutarotenone Me ether, m.p. 141°, $[\alpha]_D -130^\circ$ in C_6H_6 , which is hydrolysed (2% H_2SO_4) to mutarotenone. dl-isoRotenone forms the Me ether, m.p. 189—190°, which is also obtained from l-isorotenone and is hydrolysed to the dl-form. Methylation of (II) affords deguelin Me ether, m.p. 143—148°, hydrogenated to a substance, m.p. 155—157°. Dihydrodeguelin yields a Me ether, m.p. 152—154°. (III) is methylated to a Me_2 ether, m.p. 169—170° (also obtained from β -toxicarol), which is stable to 10% acid, but readily resinified by alkali. (During the methylation processes, substances of m.p. 182—184° and 190—192°, which may be Me ethers, have been obtained.) This Me_2 ether is reduced (Pt-H_2) to a "tetrahydro-dimethyl ether," m.p. 175—176°, also obtained by hydrogenation of the "dihydro-dimethyl ether," m.p. 176°, prepared together with Me ether, m.p. 202°, by methylation of dihydro- α -toxicarol. F. R. S.

Active sulphur compounds of Karwendol crude oil. B. REICHERT [with K. SIEWERT] (Arch. Pharm., 1938, 276, 316—327).—Treatment of the crude oil with NaOH-CaO followed by washing with dil. mineral acid and H_2O , drying over CaCl_2 , and treating the product successively with NaNH_2 and MgEtCl gives a pale yellow oil in only 20% yield. If the crude oil in light petroleum is treated with acid and then with alkali and finally with NaNH_2 a satisfactory product is secured but the yield is small and is not improved if treatment with MgEtCl and distillation over Na is substituted for treatment with NaNH_2 . The best results are obtained by use of superheated steam followed by MgEtCl on the material pretreated with HCl and NaOH. Further enrichment of this product in the active thiophen components cannot be attained by fractional distillation or by treatment with I and HgO. Cautious addition of 96% H_2SO_4 to the crude oil in light petroleum at 0° and distillation of the sulphonated product with steam gives a thiophen fraction, transformed by AcCl and AlCl_3 into an acetyldimethyl- (or ethyl)thiophen (*p*-nitrophenylhydrazones, m.p. 198—199°), which is not identical with the 5-acetyl-2-isopropylthiophen obtained by Scheibler from other bituminous tar oils. H. W.

Unsaturated sulphones. II. Oxidation, bromination, and hydrogenation of unsaturated sulphones. E. DE R. VAN ZUYDEWIJN (Rec. trav. chim., 1938, 57, 445—455).—3:4-Dimethyl- Δ^3 -thiacyclopentene 1:1-dioxide (I) oxidised with AcO_2H yields 3:4-diacetoxy- (II), m.p. 136—138°, and impure 3-hydroxy-4-acetoxy-3:4-dimethylthiacyclopentane 1:1-dioxide, m.p. 95—112°, which latter is hydrolysed (KOH-EtOH) to 3:4-epoxy- (III), m.p. 83—85°, and trans-3:4-dihydroxy-3:4-dimethylthiacyclopentane 1:1-dioxide (IV), m.p. 175—176°, and acetylated ($\text{Ac}_2\text{O-H}_2\text{SO}_4$) to (II). With EtOH-KOH (I) yields only (III). With KMnO_4 (I) yields cis-3:4-dihydroxy-3:4-dimethylthiacyclopentane 1:1-dioxide, m.p. 144—145.5°. Hydrolysis (boiling H_2O) of 3:4-dibromo-3:4-dimethylthiacyclopentane 1:1-dioxide (V) oxidised with AcO_2H yields 3:4-di-

acetoxy-, m.p. 140—142.5°, hydrolysed (H₂O) to 3:4-dihydroxy-3-methylthiacyclopentane 1:1-dioxide, m.p. 126—127°, also formed by oxidation (OsO₄-KClO₃) of (V). Oxidation of Δ³-thiacyclopentene 1:1-dioxide (VI) with AcO₂H yields trans-, m.p. 159—160°, and with KMnO₄, cis-3:4-dihydroxy-thiacyclopentane 1:1-dioxide, m.p. 129—131°. Bromination of (VI) in H₂O or CCl₄ yields cis-3:4-dibromothiacyclopentane 1:1-dioxide, m.p. 139—141°, whilst Δ⁴-thiacyclopentene 1:1-dioxide with Br in H₂O yields 4:5-dibromothiacyclopentane 1:1-dioxide, m.p. 112—115°. α-Benzylsulphonyl-Δ³-propene is oxidised (AcO₂H) to α-benzylsulphonyl-βγ-dihydroxypropane, m.p. 110—111°, and with Br in CCl₄ yields α-benzylsulphonyl-βγ-dibromopropane, m.p. 83—84°. Hydrogenation (PtO₂-H₂ in EtOH) of (VI) yields thiacyclopentane 1:1-dioxide. J. D. R.

Electrolytic reduction of N-phenylsuccinimide. B. SAKURAI (Bull. Chem. Soc. Japan, 1938, 13, 350—352).—Reduction of the imide, using a low c.d. and Pb cathode in 90% H₂SO₄, and then a high c.d. and Zn-Hg cathode in 50% H₂SO₄, yields N-phenylpyrrolidine. A. Li.

Pyrrole derivatives. I. J. RINKES (Rec. trav. chim., 1938, 57, 423—426).—NH₂·CH₂·CHO and CH₃Ac·CO·CO₂Et in aq. NaOH yield 3-acetylpyrrole-2-carboxylic acid, m.p. 192°, converted by Cu chromate in boiling quinoline into 3-acetylpyrrole, m.p. 115—116°. NH₂·CH₂·CHO and CO₂Me·CH₂·CO·CO₂Me in aq. KOH yield 3-carbomethoxypyrrole-2-carboxylic acid, m.p. 201°. CHO·CHNa·CO₂Me (from Na, MeOAc, and HCO₂Me in xylene) with NH₂·CH₂·CHO yields 3-carbomethoxypyrrole, which is nitrated to the Me ester, m.p. 204°, of 2-nitropyrrole-4-carboxylic acid, m.p. 226°, nitration of which gives 2:4-dinitropyrrole. J. D. R.

Synthesis of local anæsthetics. III. S. BAGCHEE, K. N. GAIND, and J. N. RAY (J.C.S., 1938, 657—659).—Me α-bromo-β-hydroxy-β-phenylpropionate, m.p. 64°, and the Et, Pr, Pr^{is}, Bu, Bu^{is}, isoamyl, and benzyl esters (viscous liquids) have been prepared. The α-Br-esters with piperidine in C₆H₆ yield the α-piperidino-esters: Me, m.p. 142°, Pr (viscous liquid), Pr^{is}, m.p. 111°, Bu^{is}, isoamyl, m.p. 86°, and benzyl (hydrochlorides, m.p. Me 182°, Bu^{is} 141°, isoamyl 159°, benzyl 187°). These esters with BzCl in C₆H₆ give the α-piperidino-β-benzoyloxy-ester hydrochlorides: Me, m.p. 101°, Et, m.p. 127°, Pr, m.p. 112°, Pr^{is}, m.p. 190° (decomp.), Bu, m.p. 118°, Bu^{is}, m.p. 82°, isoamyl, m.p. (free base) 79°, benzyl, m.p. 175°. Pr^{is} α-piperidino-β-cinnamoyloxy-β-phenylpropionate hydrochloride and the β-β'-phenylpropionoxy Me ester hydrochloride have m.p. 223° and 197°, respectively. p-Nitrocinnamic acid and Br vapour in aq. Na₂CO₃ yield ω-bromo-p-nitrostyrene and α-bromo-β-hydroxy-β-p-nitrophenylpropionic acid, m.p. 179°, the Et ester, m.p. 95°, of which affords the α-piperidino-ester [hydrochloride, m.p. 205° (decomp.)], the Bz derivative, m.p. 139° (hydrochloride, m.p. 193°), of which is reduced (PtO₂) to Et α-piperidino-β-benzoyloxy-β-p-aminophenylpropionate [dihydrochloride, m.p. 113° (decomp.)]. Me, m.p. 187°, Pr, m.p. 147°, and Pr^{is}, m.p. 181°, α-

diethylamino-β-hydroxy-β-phenylpropionate hydrochloride were also prepared. A. Li.

Pyrrolidines, piperidines, and hexahydroazepines from glycols. R. M. HILL and H. ADKINS (J. Amer. Chem. Soc., 1938, 60, 1033—1035).—5-, 6-, and 7-Membered ring bases are prepared, usually in good yield, from the appropriate glycols and CH₂Ph·CH₂·NH₂ or n-C₅H₁₁·NH₂ with Cu-Cr₂O₃ in dioxan-H₂ at 250°. The following are thus obtained: 3-, b.p. 82—85°/24 mm. (picrate, m.p. 134—135°), 2-, b.p. 96—97°/41 mm. (picrate, m.p. 114—115°), and 2:5-di-methyl-1-n-amylypyrrolidine, b.p. 105—107°/43 mm. (picrate, m.p. 95—96°); 3-, b.p. 136—137°/17 mm. (picrate, m.p. 163—164°), 2-, b.p. 132—133°/16 mm. (picrate, m.p. 141—142°), and 2:5-di-methyl-1-β-phenylethylpyrrolidine, b.p. 106—108°/2 mm. (picrate, m.p. 131—132°); 2-methyl-1-n-amyly-, b.p. 104—105°/23 mm. (picrate, m.p. 94—95°), and 1-β-phenylethyl-piperidine, b.p. 148—149°/27 mm. (picrate, m.p. 118—119°); 2-methyl-1-n-amyly-, b.p. 117—118°/22 mm. (picrate, m.p. 79—80°), 2-methyl-1-β-phenylethyl-, b.p. 106—109°/1 mm. (picrate, m.p. 105—106°), and 3:6-diethyl-1-n-amyly-hexahydroazepine [-hexamethyleneimine], b.p. 98—100°/2 mm. The necessary glycols were prepared by Cu-Cr₂O₃ hydrogenation in dioxan or EtOH at 200—300 atm. as follows: γ,δ-di(hydroxymethyl)octane, b.p. 133—134°/1 mm. (phenylurethane, m.p. 135—136°; with MgMeI gives 2CH₃), from [CH₂·CEt(CO₂Et)]₂ [prep. from CEtNa(CO₂Et)₂ and (CH₂Br)₂ in boiling xylene], m.p. 95—96°, at 250°; heptane-α,ε-diol, b.p. 94—97°/1 mm. (phenylurethane, m.p. 97—98°), from COMe·[CH₂]₃·CO₂Et at 250°; hexane-α,ε-diol, b.p. 89—91°/0.5 mm., from COMe·[CH₂]₃·CO₂Et, at 250°; hexane-β,ε-diol, b.p. 85—87°/1 mm., from COMe·CH₂·COMe at 160—170°. R. S. C.

Direct chlorination of pyridine. Z. RODEWALD and E. PĚAŽEK (Rocz. Chem., 1938, 18, 39—43).—Cl₂ passed through fused C₅H₅N·HCl at 200° yields 3-chloro- and 3:5-dichloro-pyridine, m.p. 66°, identified by conversion into the corresponding amines (40—80 hr. at 200° with conc. aq. NH₃). R. T.

Long-chain alkylpyridines and their derivatives. New examples of liquid crystals. G. A. KNIGHT and B. D. SHAW (J.C.S., 1938, 682—683).—The following compounds have been prepared by Tschitschibabin's method (A., 1936, 734), carried out at 100° (the hydrochlorides form liquid crystals): 1-dodecylpyridinium chloride, m.p. I, 71°, II, 145°, bromide, m.p. I, 89—90°, II, 125°, and iodide, m.p. I, 88—89°, II, 93°; 1-tetradecylpyridinium chloride, m.p. I, 77°, II, 205°, and iodide, m.p. I, 94°, II, 155°; 1-cetylpyridinium chloride, m.p. I, 83°, II, 217° (lit. 110°), and iodide, m.p. I, 98°, II, 205° (lit. 101°); 1-octadecylpyridinium chloride, m.p. I, 89°, II, 220°, and iodide, m.p. I, 103°, II, 221°; 2-n-tridecylpyridine, m.p. 19°, b.p. 199°/10 mm. (hydrochloride, m.p. I, 52°, II, 109°; picrate, m.p. 78°; picrolonate, m.p. 85°); 2-n-pentadecylpyridine, m.p. 29°, b.p. 215°/10 mm. (hydrochloride, m.p. I, 59°, II, 118°; picrate, m.p. 85°; picrolonate, m.p. 92°); 2-n-heptadecylpyridine, m.p. 37°, b.p. 231°/10 mm. (hydrochloride, m.p. I, 65°, II, 125°; picrate, m.p. 85—86°; picrolonate, m.p. 95—5°);

and 2-n-nonadecylpyridine, m.p. 46°, b.p. 247—248°/10 mm. (hydrochloride, m.p. I, 73°, II, 134°; picrate, m.p. 93—94°; picrolonate, m.p. 99—100°). F. R. S.

Fission of the furan ring by primary aromatic amines and hydrogen chloride. W. BORSCHKE, H. LEDITSCHKE and K. LANGE (Ber., 1938, **71**, [B], 957—966).—Pyromuconitrile (I) is transformed by resorcinol, ZnCl_2 , and HCl in Et_2O into the corresponding ketimine hydrochloride, converted by boiling H_2O into 2:4-dihydroxyphenyl 2-furyl ketone (II), m.p. 128° [2:4-dinitrophenylhydrazone, m.p. 257° (decomp.); 3:5-dibenzeneazo-2:4-dihydroxyphenyl 2-furyl ketone, m.p. 240—241°; the dibenzeneazo-derivatives of resacetophenone and 2:4-dihydroxybenzophenone have m.p. 220° and 226°, respectively]. With Br in AcOH (II) gives 3:5-dibromo-2:4-dihydroxyphenyl 2-furyl ketone, m.p. 117°; with CH_2N_2 in Et_2O and BzCl in $\text{C}_5\text{H}_5\text{N}$ (II) yields 2-hydroxy-4-methoxyphenyl 2-furyl ketone, m.p. 92°, and 2-hydroxy-4-benzoyloxyphenyl 2-furyl ketone, m.p. 109°. From (I) and the requisite Grignard reagent are derived 2-acetyl- (III), b.p. 168—169°/760 mm., m.p. 30—32° (2:4-dinitrophenylhydrazone, m.p. 158°), 2-propionyl-, b.p. 75—80°/12 mm., m.p. 28—29° (2:4-dinitrophenylhydrazone, m.p. 163°), and 2-phenacetyl-, b.p. 150—154°/15 mm., m.p. 47° (2:4-dinitrophenylhydrazone, m.p. 179°) furan. PhCHO , (III), and NaOH afford 2-cinnamoylfuran, m.p. 88—90°, reduced (Pd-C in MeOH) to 2- β -phenylpropionylfuran, b.p. 185°/12 mm. (2:4-dinitrophenylhydrazone, m.p. 165°). The 2-acylfurans are converted by NH_2Ph and $\text{NH}_2\text{Ph.HCl}$ in EtOH at 100—110° into the corresponding pyridinium compounds. Thus are obtained 3-hydroxy-1:2-diphenylpyridinium hydroxide, m.p. (indef.) about 130° (corresponding hydrochloride, platinichloride, decomp. 236°, and picrate, m.p. about 221°; 3-acetoxy-1:2-diphenylpyridinium picrate, m.p. 163°, with some 2-benzoyl-1-phenylpyrrole, m.p. 116°; 3-hydroxy-1-phenyl-2-p-tolylpyridinium hydroxide (+ H_2O), m.p. 132—133° (picrate, m.p. 214°; picrate of the Ac derivative, m.p. 171°), and 2-p-toluyl-1-phenylpyrrole; 3-hydroxy-1-phenyl-2-p-anisylpyridinium hydroxide, m.p. 152° (corresponding hydrochloride and picrate, m.p. 196°), and 2-p-anisoyl-1-phenylpyrrole, m.p. 119° (two isomeric 2:4-dinitrophenylhydrazones, m.p. 212—213° and 153—154°, respectively); 3-hydroxy-2-veratroyl-1-phenylpyridinium picrate, m.p. 128°. Fural is converted by NH_2Ph and $\text{NH}_2\text{Ph.HCl}$ in boiling EtOH into 3-hydroxy-2-furoyl-1-phenylpyridinium picrate, m.p. 249° (decomp.), and by $p\text{-OMe.C}_6\text{H}_4\text{.NH}_2$ into 3-hydroxy-2-furoyl-1-p-anisylpyridinium picrate, m.p. 187°. The picrates of 3-hydroxy-1-phenyl-2-methyl-, m.p. 162°, -2-ethyl-, m.p. 175°, -2-benzyl-, m.p. 179°, and -2- β -phenylethyl-, m.p. 194°, pyridinium are described. By means of the requisite amine and amine hydrochloride the following picrates are obtained: 3-hydroxy-2-phenyl-1-p-anisyl-, m.p. 229°, -1-p-bromophenyl-, m.p. 187°, -1-p-nitrophenyl-, m.p. 220°, -1-m-nitrophenyl-, m.p. 243°, and -1-o-tolyl-, m.p. 225°, pyridinium. 3-Hydroxy-2-phenyl-1-p-hydroxyphenylpyridinium hydroxide has m.p. >280°. Furfuraldehyde (IV), NH_2Ph , $\text{NH}_2\text{Ph.HCl}$ and MeOH at 100° yield 3-hydroxy-1-phenylpyridinium chloride, m.p. 211—212°, converted

by evaporation of its aq. solution with NaOH or Na_2CO_3 into the hydroxide (corresponding picrate, m.p. 208°) and by distillation with Na_2CO_3 into NH_2Ph . 3-Acetoxy-1-phenylpyridinium picrate has m.p. 165°. $p\text{-NH}_2\text{.C}_6\text{H}_4\text{.OH}$, (IV), and $p\text{-NH}_2\text{.C}_6\text{H}_4\text{.OH.HCl}$ in MeOH at 40° yield δ -p-hydroxyphenylamino- α -hydroxy- $\Delta^{\alpha\gamma}$ -pentadienal-p-hydroxyanil hydrochloride, m.p. 188°, or 3-hydroxy-1-p-hydroxyphenylpyridinium chloride, m.p. 264° (corresponding picrate, m.p. 228°), when heated in a sealed tube. δ -o-Hydroxyphenylamino- α -hydroxy- $\Delta^{\alpha\gamma}$ -pentadienal-o-hydroxyanil hydrochloride has m.p. 163—164°.

II. W.

Compound from nicotinamide and acetobromoglucose.—See B., 1938, 731.

Induced asymmetry and optical resolution of 2-phenylpyridine derivatives. J. G. BRECKENRIDGE and O. C. SMITH (Canad. J. Res., 1938, **16**, B, 109—113).—The following salts of 2-phenylpyridine-2':3-dicarboxylic acid (I) show an optical rotation (vals. in CHCl_3 given in parentheses), ascribed to asymmetry induced by the alkaloid, in the opposite direction to that of the free alkaloid (cf. "Kuhn's effect," A., 1927, 876): quinine ($[\alpha]_{5461}^{22} + 244^\circ$, $[\alpha]_{5780}^{22} + 209^\circ$, $[\alpha]_{4358}^{22} + 476^\circ$), quinidine ($[\alpha]_{5461}^{22} - 206^\circ$, $[\alpha]_{5780}^{22} - 175^\circ$, $[\alpha]_{4358}^{22} - 412^\circ$), cinchonine ($[\alpha]_{5461}^{22} - 250^\circ$, $[\alpha]_{5780}^{22} - 211^\circ$, $[\alpha]_{4358}^{22} - 516^\circ$), cinchonidine ($[\alpha]_{5461}^{22} + 303^\circ$, $[\alpha]_{5780}^{22} + 259^\circ$, $[\alpha]_{4358}^{22} + 617^\circ$). A solution of quinidine and (I) in 95% EtOH mutarotated -0.25° within 3 min. of wetting. The methiodide, m.p. 151° (corr.), of the Me_2 ester of (I) with Ag bromocamphorsulphonate in $\text{MeOH-H}_2\text{O}$ gives the corresponding bromocamphorsulphonate, m.p. 210°, $[\alpha]_{5461}^{22} + 107^\circ$ in CHCl_3 , $+83^\circ$ in EtOH , from which the d-methiodide, m.p. 151°, $[\alpha]_{5461}^{22} + 156.7^\circ$ in CHCl_3 , was obtained. The rotation remained unchanged when the EtOH solution was heated for 3 hr. at 70°. H. G. M.

Dimethyloxindoles. A. WAHL and V. LIVOVSKI (Bull. Soc. chim., 1938, [v], 5, 653—666; cf. A., 1938, II, 111).—Cyclisation of 2:5- and 2:4-dimethylchloroacetanilides with AlCl_3 affords a dimethyloxindole, m.p. 159°, b.p. 205—210°/15 mm., and an isomeride, m.p. 153° (loc. cit.), respectively, but the structures are not certain, as wandering of Me may occur; e.g., 2:6-dimethylchloroacetanilide yields a dimethyloxindole, m.p. 170°. Modifications are recorded of Wispek's synthesis of 5:7-dimethyloxindole, m.p. 234° (CHPh : derivative, m.p. 235°; isoindigotin derivative). Oxindole (I) (1 mol.) [isatin-oxime, new m.p. 266° (decomp.)] and COMe_2 (1 mol.) in HCl yield the COMe_2 derivative, m.p. 186°, but 2 mols. of 5- and 7-methyloxindole (II) react with 1 mol. of COMe_2 . $\text{CO(NH}_2)_2$ forms additive compounds, m.p. 162° and 180°, respectively, with (I) and (II) in EtOH . A. T. P.

[Biogenesis of the isoquinoline alkaloids. Synthesis of 6:7-dihydroxy-1-methyl-1:2:3:4-tetrahydroisoquinoline under physiological conditions.] C. SCHÖPF and H. BAYERLE (Annalen, 1938, **534**, 297).—6:7-Dimethoxy-1-methyl-1:2:3:4-tetrahydroisoquinoline picrate has m.p. 199—201° when rapidly heated; this val. is practically identical with that of Späth *et al.* (A., 1938, II, 117).

H. W.

Alkoxyquinoline compounds with anæsthetic action. H. WOJAHN and H. KRAMER (Arch. Pharm., 1938, 276, 291—302).—2-Chloro-4-cyanoquinoline is readily converted by NaOMe in MeOH into 4-cyano-2-methoxyquinoline, m.p. 134°. The following 4-cyanoquinolines are analogously prepared: 2-propoxy-, m.p. 58°; 2-isopropoxy-, m.p. 73°; 2-isobutoxy-, m.p. 84°; 2- α -methylpropoxy-, b.p. 175°/16 mm., m.p. 84°; 2-tert-butoxy-, b.p. 178°/12 mm., m.p. 80°; 2-isoamyloxy-, b.p. 197°/15 mm. The nitriles are reduced (H_2 -Pd-BaSO₄ in AcOH at about 40°) to the following 2-alkoxy-4-aminomethylquinolines: 2-methoxy-, m.p. 89° (mono-, m.p. 205°, and di-, m.p. >250°, -hydrochloride); 2-propoxy-, m.p. 48° (monohydrochloride, m.p. 217°); 2-isopropoxy-, m.p. 61° (monohydrochloride, m.p. 219°); 2-isobutoxy-, b.p. 226°/15 mm., m.p. 44° (monohydrochloride, m.p. 223°); 2- α -methylpropoxy-, m.p. 70° (monohydrochloride, m.p. 214°); 2-isoamyloxy-, b.p. 205°/15 mm. (monohydrochloride, m.p. 207°). 2-Chloroquinoline-3-carboxylamide (I) is converted by NaOAlk in AlkOH into the following 2-alkoxyquinoline-3-carboxylamides: 2-methoxy-, m.p. 172°; 2-ethoxy-, m.p. 157.5°; 2-butoxy-, m.p. 137°. These are transformed by KOBBr into 2-chloro-, m.p. 170.5°, 2-methoxy-, m.p. 87.5°, 2-ethoxy-, m.p. 75°, and 2-butoxy-, m.p. 84°, -3-aminomethylquinoline. Boiling SOCl₂ transforms (I) into 2-chloro-3-cyanoquinoline, m.p. 166.5°, whence 3-cyano-2-methoxy-, b.p. 228°/37 mm., m.p. 74°, -2-ethoxy-, b.p. 178°/12 mm., m.p. 74°, -2-propoxy-, b.p. 178°/13 mm., m.p. 58°, -2-isopropoxy-, m.p. 178°/14 mm., m.p. 57°, and 2-butoxy-, b.p. 202°/12 mm., m.p. 54°, -quinoline. These are reduced to 2-methoxy-, b.p. 178°/13 mm., m.p. 85° (monohydrochloride, m.p. 195°; monopicate, m.p. 218°); 2-ethoxy-, b.p. 186°/13 mm., m.p. 82° (monohydrochloride, m.p. 108°), and 2-butoxy-, b.p. 205°/9 mm. (monohydrochloride, m.p. 186°), -3-aminomethylquinoline, respectively. 2-Chloroquinoline-3-carboxyl chloride, m.p. 172°, from the acid and boiling SOCl₂, with NHEt₂ in C₆H₆ at 100° affords 2-chloroquinoline-3-carboxydiethylamide, which with NaOAlk in AlkOH yields respectively 2-methoxy-, b.p. 222°/13 mm., m.p. 81°, 2-propoxy-, b.p. 232°/11 mm., 2-isopropoxy-, b.p. 221°/11 mm., and 2-butoxy-, b.p. 233°/13 mm., -quinoline-3-carboxydiethylamide. β -Diethylaminoethyl 2-ethoxyquinoline-3-carboxylate, b.p. 188°/1 mm., and its monohydrochloride, m.p. 164°, are described. 2-Butoxyquinoline-3-carboxylic acid, m.p. 81.5°, and its β -diethylaminoethyl ester, b.p. 230°/6 mm. (hydrochloride, m.p. 145°), have been prepared. H. W.

Catalytic condensation of acetylene with aromatic amines. XVI. Simultaneous condensation of aniline, toluidines, and acetone with acetylene in presence of cuprous chloride. N. KOZLOV (J. Gen. Chem. Russ., 1938, 8, 366—369).—2:4-Dimethyl-, 2:4:6- or 2:4:7-trimethylquinoline is obtained from NH₂Ph, *p*- or *m*-toluidine, COMe₂, and C₂H₂, in presence of CuCl. R. T.

Structure of the quinaldinic acids. V. M. MITCHOVITCH (Compt. rend., 1938, 206, 1261—1262).—Isatic acid with CH₃Ac-CO₂Et or CO(CH₂-CO₂H)₂ (cf. A., 1898, i, 207, 683) affords the same quinaldine-3:4-dicarboxylic acid, which loses

1 H₂O at 100°/0.05 mm.; the K₂ salt with Me₂SO₄-MeOH affords the Me₂ ester, m.p. 61—62° (picrate, m.p. 156°). J. L. D.

New cases of reversible migration of acyl from oxygen to nitrogen. Synthesis of 3-methylisoquinolines. E. VINKLER and V. BRUCKNER (J. pr. Chem., 1938, [ii], 151, 17—24).— β -Nitro- α -3:4-dimethoxyphenylpropyl alcohol and the acyl halide in C₅H₅N give the oily benzoate, anisate, veratrate, and phenylacetate. If these esters are reduced electrolytically and the products pptd. from aq. acid by Na₂CO₃, the acyl wanders from the O to the N; thus are obtained β -benz-, -anis-, -veratr-, and -phenylacet-amido- α -3:4-dimethoxyphenylpropyl alcohol (I). With PCl₅-POCl₃ in hot xylene (I) gives 6:7-dimethoxy-1-benzyl-3-methylisoquinoline, but this method of synthesis is not economical. R. S. C.

Syntheses in the 2-phenylquinoline series. III. Interaction of ethyl 2-phenylquinoline-4-carboxylate and Grignard's reagents. K. FEIST, W. AWE, M. KUKLINSKI, and W. VÖLKSEN (Arch. Pharm., 1938, 276, 271—279).—Et 2-phenylquinoline-4-carboxylate (I) is converted by MgMeI in Et₂O into 2-phenyl-4-quinolyldimethylcarbinol (+1H₂O), m.p. 131° (picrates I and II, m.p. 199° and 190°, respectively). Similarly 2-phenyl-4-quinolyldibenzylcarbinol, m.p. 127° (also +1H₂O) (picrate, m.p. 147°), and 2-phenyl-4-quinolyldi-*m*-tolylcarbinol, m.p. 197° [picrate (+4H₂O), m.p. 126°], are obtained from (I) and CH₂Ph-MgCl or *m*-C₆H₄Me-MgBr, respectively. The production of ketones is not observed. 4-Cyano-2-phenylquinoline is readily converted by MgEtBr into 2-phenyl-4-quinolyl Et ketone, m.p. 114° (picrate, m.p. 182°; semicarbazone, m.p. 211—212°). 2-Phenyl-4-quinolyl CH₂Ph ketone, m.p. 104° (picrate, m.p. 178°), is obtained in poorer yield and is transformed with difficulty into its oxime, m.p. 134°. (I) and Mg pyrrol iodide afford 2-phenyl-4-quinolyl 2-pyrrol ketone, m.p. 177° (picrate, m.p. 238°). (I) and Mg carbazyl iodide give a product, C₂₈H₁₈ON₂, m.p. 164°; under ultra-violet light this is shown to consist in part of violet fluorescent crystals which have m.p. 156°. A cryst. picrate could not be obtained. H. W.

Preparation and reactions of 4-arylamino-2-arylquinolines. K. DZIEWOŃSKI, W. GUMUŁKA, and J. MOSZEWSKI with (in part) L. BERNACIŃSKI, J. BOLESŁAWICZ, S. SULEKO, H. KRAGEN, and M. KOZAKIEWICZ (Bull. Acad. Polonaise, 1937, A, 555—570).—CS(NH-C₆H₄-OMe-*p*)₂ (I) and CPhMe at 180—220° give 4-*p*-anisidino-6-methoxy-2-phenylquinoline, m.p. 204.5° [hydrochloride, m.p. 294° (decomp.); picrate, m.p. 224° (decomp.); compound with (CH₂Br)₂, m.p. 270° (decomp.); NO-, m.p. 218° (decomp.)], and Ac derivative, m.p. 163°, reduced by Na-C₅H₁₁OH to the 1:2:3:4-H₄-derivative, m.p. 160°, and converted by KOH-EtOH at 200° or slowly by HI-AeOH into 4-*p*-hydroxyanilino-6-hydroxy-2-phenylquinoline, m.p. 217°, and by KOH alone at 240—260° into 4-hydroxy-6-methoxy-2-phenylquinoline, +2H₂O, m.p. 163° (decomp.), and anhyd., m.p. 293°. CPhMe and CS(NH-C₆H₄-OEt-*p*)₂ at 130—270° give 4-*p*-phenetidino-6-ethoxy-2-phenylquinoline, m.p. 155—156° [hydrochloride, m.p. 285.5° (decomp.); picrate, m.p. 227.5°; methiodide, m.p. 267—268°

(decomp.); *Ac*, m.p. 134.5—135.5°, and *NO*-derivative [*acetate*, m.p. 143—144° (decomp.)]. *p*-*OMe*-C₆H₄·*COME* and (I) at 180—240° give 4-*p*-*anisidino*-6-*methoxy*-2-*p*-*anisylquinoline*, m.p. 164° [*hydrochloride*, m.p. 274—275° (decomp.)]; *picrate*, m.p. 262° (decomp.); *NO*-, m.p. 209—210° (decomp.), and *Ac* derivative, m.p. 162.5—163.5°, which is hydrolysed and reduced by Na-C₅H₁₁·OH to 6-*methoxy*-2-*p*-*anisyl*-1:2:3:4-*tetrahydroquinoline*, m.p. 106.5—107.5°, and is converted by HI-AcOH into 4-*hydroxy*-6-*methoxy*-2-*p*-*hydroxyphenyl*- or 4:6-*di*-*hydroxy*-2-*p*-*anisylquinoline*, m.p. 347° (after decomp.). 4-*Anilino*-2- α - [*methiodide*, m.p. 296° (decomp.)]; *ethiodide*, m.p. 275—276° (decomp.); *N*'-*Me*, m.p. 231—232°, and -*Et* derivative, m.p. 257°, and - β -*naphthylquinoline* [*hydrochloride*, m.p. 264°, *picrate*, m.p. 195° (decomp.)]; *N*'-*Me*, m.p. 222°, *NO*-, m.p. 206° (decomp.), and *Ac* derivative, m.p. 163°] are hydrolysed by 30% KOH-EtOH at 200° to 4-*hydroxy*-2- α -, m.p. 281° [*picrate*, m.p. 185° (decomp.)], and - β -*naphthylquinoline*, m.p. 291°. R. S. C.

Attempted photo-oxidation in the acridine series. C. DUFRAISSE and J. HOUPIILLART (Bull. Soc. chim., 1938, [v], 5, 626—633).—Photo-oxides cannot be obtained from acridine (I) or its 9-Ph derivative. The absorption spectra of (I) and anthracene, and of their 9-Ph derivatives, are compared. A. T. P.

5-Hydroxyphenanthroline. J. S. TURSKI and H. KLEJN (Rocz. Chem., 1938, 18, 31—35).—2:4:1-C₆H₃(NO₂)₂·OH, SnCl₄, Zn, and HCl yield 2:4:1-C₆H₃(NH₂,HCl)₂·OH, SnCl₄, converted by the Skraup reaction into 5-*hydroxyphenanthroline*, m.p. 157° (*sulphate*). R. T.

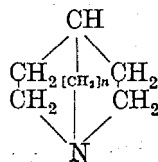
Benzquinolines.—See B., 1938, 701.

Synthesis of compounds with hypnotic properties. II. Phenoxyethylhydantoins. W. B. WHITNEY with H. R. HENZE (J. Amer. Chem. Soc., 1938, 60, 1148—1151; cf. A., 1936, 613).—NaOPh and CH₂Cl·OMe in PhMe give 16% of *phenoxyacetone*, b.p. 110—112°/12 mm. (*semicarbazone*, m.p. 176°). OPh·CH₂·COCl and ZnEtI give mainly OPh·CH₂·CO₂Ph and OPh·CH₂·CET₃·OH (I). OPh·CH₂·CO·NH₂ with MgEtI gives mainly (I), but with P₂O₅ gives *phenoxyacetonitrile*, b.p. 128°/17 mm., which with MgRBr gives usually moderate yields of *phenoxyethyl Et*, b.p. 98—100°/5 mm., *Pr*^a, b.p. 112°/4 mm. (m.p. 108.5°), *Bu*^a, b.p. 130°/4 mm. (m.p. 76°), *sec*·*Bu*, b.p. 117°/4 mm. (an oil), *n*-, b.p. 153°/10 mm. (m.p. 87.5—88°), and *iso*-*amyl ketone*, b.p. 140°/10 mm. (m.p. 83.5—84°), and ω -*phenoxyacetophenone*, b.p. 187°/8 mm. (m.p. 187—187.5°); m.p. in parentheses are those of the *semicarbazones*. V.p. of the ketones are determined and latent heats of vaporisation are calc. The ketones with KCN and (NH₄)₂CO₃ in 50% EtOH give 5-*phenoxyethyl*-5-*methyl*- (I), m.p. 147°, -*ethyl*-, m.p. 176°, -*n*-*propyl*-, m.p. 149°, *n*-, m.p. 162°, and *sec*·*butyl*-, m.p. 195°, -*n*-, m.p. 166°, and -*iso*-*amyl*-, m.p. 181.5°, and -*phenyl-hydantoin*, m.p. 181°, which are hypnotics. Me₂SO₄, NaOEt, and (I) give 1:3:5-*trimethyl*-5-*phenoxyethylhydantoin*, m.p. 81—83°. Temp. are corr. R. S. C.

Raman effect and problems of constitution. XI. Glyoxaline. K. W. F. KOHLRAUSCH and R. SEKA (Ber., 1938, 71, [B], 985—991).—The Raman spectra of glyoxaline (I), 2- and 1-methyl- and 5-chloro-1-methyl-glyoxaline, of benzimidazole and its 1- and 2-methyl derivatives have been measured. It is pointed out that the results obtained with open-chain derivatives cannot be directly applied to heterocyclic compounds. Comparison is made with pyrazole, pyrrole, thiophen, furan, *cyclopentadiene*, 2-methyl-pyrrole, -furan, and -thiophen, and 1-methyl-pyrrole. It is suggested that the imide-H of (I) is shared between the two N atoms. At present, the Raman spectra do not give unequivocal evidence of the structure of heterocyclic compounds. H. W.

Wood's light and derivatives of carbamide and pyrazole. P. ANTONIO (Boll. Chim. farm., 1938, 77, 209—212).—The fluorescence colours (mainly blue-violet) of various CO(NH₂)₂ and pyrazole derivatives (alone or as therapeutic mixtures) irradiated with ultra-violet light (365 m μ .) are tabulated. F. O. H.

Formation of dicyclic amines with nitrogen as branching atom. V. PRELOG, E. CERKOVNIKOV, and G. USTRICEV (Annalen, 1938, 535, 37—46).—4-Aminomethyltetrahydropyran [*hydrochloride*, m.p. 194—194.5° (corr.)]; *hydrobromide* (I), m.p. 202—203° (corr.)] is best obtained (yield 52.5%) from tetrahydropyran-4-acetic acid by the Curtius-Schmidt process; it results (10% yield) by reduction of 4-cyanotetrahydropyran with Cr(OH)₂ or (20% yield) with H₂ in presence of Pt. 4-Bromomethyltetrahydropyran gives 4-*phthalimidomethyltetrahydropyran*, m.p. 128° (corr.), in 21% yield, whence the base in good yield. 69% HBr at 100° converts (I) into $\alpha\epsilon$ -*dibromo- γ -aminomethylpentane*. *hydrobromide*, m.p. 182—183° (corr.), which with 0.1N-NaOH at 50° gives *dicyclo*-[1:2:2]-*aza*-1-heptane (A; *n* = 1) [*picrate*, m.p. 285° (corr.)] in 83.5% yield. Tetrahydropyran-4-propionic acid is converted similarly into 4- β -*aminomethyltetrahydropyran*, b.p. 88—89°/13 mm., the *hydrobromide*, m.p. 144° (corr.), of which is transformed by 69% HBr at 100° into $\alpha\epsilon$ -*dibromo- γ - β -aminoethylpentane* *hydrobromide*, m.p. 175—176° (corr.); this readily affords quinuclidine (A; *n* = 2) (*picrate*, m.p. 275—276°). Tetrahydropyran-4-carboxylic acid gives 4-*amino*tetrahydropyran, b.p. 52—53°/13 mm., the *hydrobromide*, m.p. 190—191° (corr.), of which yields $\alpha\epsilon$ -*dibromo- γ -aminopentane* *hydrobromide*, m.p. 182—183° (corr.), from which a dicyclic base could not be derived. OEt·[CH₂]₂·OH is transformed by PhSO₂Cl and NaOH into β -*ethoxyethyl benzenesulphonate*, b.p. 180—190°/10 mm. (slight decomp.), which with 1-phenylpiperazine in boiling C₆H₆ gives 1-*phenyl*-4- β -*ethoxyethylpiperazine*, b.p. 190—193°/10 mm. This is transformed by HNO₃ followed by SO₂ and NaOH into 1- β -*ethoxyethylpiperazine*, b.p. about 100°/10 mm. (*platinichloride*), which, with 76% HBr at 100—110°, yields 1- β -*bromoethylpiperazine* [*picrate*, m.p. 257°; *hydrobromide*, m.p. 240° (decomp.); *hydrochloride*, m.p. 273° (corr.; decomp.); *platinichloride*, m.p.



(A.)

281—282° (corr.; decomp.) and 1- β -hydroxyethylpiperazine [picrate, m.p. 247—248° (corr.); hydrochloride, m.p. 182—183° (corr.); platinichloride, decomp. 248° after blackening at 238°]. H. W.

2-Alkylthiol-5-alkyl- and -5:5-dialkyl-barbituric acids. J. LEE (J. Amer. Chem. Soc., 1938, 60, 993—996).—With alkyl halides in abs. EtOH or Me₂SO₄ in aq. NaOH 5-alkyl-2-thiobarbituric acids give first the relatively stable *S*-ethers and then the unstable 2-alkylthiol-5:5-dialkylbarbituric acids. 5-isopropyl-2-thiobarbituric acid (I) [prep. in 82% yield from CHPr³(CO₂Et)₂, CS(NH₂)₂, and NaOEt—EtOH], m.p. 172—173°, thus gives 2-methyl-, m.p. 247—248° [with H₂O₂—Pb(OAc)₄ gives 5-isopropylbarbituric acid], and 2-allyl-thiol-5-isopropylbarbituric acid, m.p. 224—225°, and thence 2-allylthiol-5-methyl-5-isopropyl-, m.p. 162—163°, 2-methylthiol-5-ethyl-5-isopropyl-, m.p. 133—134°, 5-isopropyl-5-allyl-, m.p. 122.5—123°, and 5-isopropyl-5-isoamyl-barbituric acid, m.p. 130—130.5°. CH₃Et(CO₂Et)₂ gives only 1% of 5-ethyl-2-thiobarbituric acid, m.p. 173—174°. With 2-chlorocyclohexanone and a trace of Cu in *N*-NaOH (I) gives 2-cyclohexanonylthiol-5-isopropylbarbituric acid, m.p. >275°. None of the products produces narcosis when injected intravenously into rabbits. The last three 5:5-dialkyl derivatives named have depressant and strychnine-like effects. R. S. C.

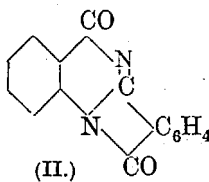
Two forms of 5:5-diisobutenylbarbituric acid. O. SCHALES (Ber., 1938, 71, [B], 1116—1117; cf. Schales, A., 1937, II, 81; Doran *et al.*, *ibid.*, 468).—5:5'-Diisobutenylbarbituric acid has m.p. 209°. Occasionally a labile modification, m.p. 222°, is formed which gradually passes into the stable variety, m.p. 209°. H. W.

Nucleic acids. VIII. Constitution of thymonucleic acid. Diphosphates of pyrimidine-deoxyribose-nucleosides. H. BREDERECK and G. CARO (Z. physiol. Chem., 1938, 253, 170—184; cf. A., 1938, III, 532).—By hydrolysis of thymonucleic acid by the methods of Thannhauser and Blanco (A., 1927, 268) and Levene and Jacobs (A., 1912, i, 926) a thymine deoxyribose monophosphoric acid (Ba and brucine salts) together with only very small amounts of one or two corresponding diphosphoric acids (brucine salts) are obtained. Hence it is improbable that thymonucleic acid and other polynucleotides are diphosphates of pyrimidine-nucleotides. W. McC.

Compounds of skatole with benzaldehyde. II. V. DOSTÁL (Chem. Listy, 1938, 32, 161—165; cf. A., 1938, II, 158).—Phenylbis-(3-methyl-2-indolyl)methane in aq. EtOH—Et₂O, NaNO₂, and HCl (at the b.p.) yield phenyl-3-methyl-2-indolyl-2'-hydroxy-3'-methyl-2'-indolylmethane *N*'-hydrochloride (I), sintering at 180°, m.p. 200° (decomp.), from which the corresponding base, m.p. 180—205° (indef.), is obtained. A solution of the base in COMe₂ gives the *N*'-hydrate, m.p. 150° (decomp.), when evaporated to dryness with aq. NH₃. In aq. COMe₂—EtOH (I), NaNO₂, and HCl yield phenyl-2-hydroxy-3-methyl-2-indolyl-3'-methyl-2'-indolylcarbinol, m.p. 190—200° (decomp.), which with NaOH in EtOH gives phenyl-3-methyl-2-indolyl-1'-hydroxy-3'-methyl-2'-indolylcarbinol, sintering at 200°, decomp. at 240°, and with HCl in COMe₂ gives

phenyl-3-methyl-2-indolide-2'-hydroxy-3'-methyl-2'-indolylmethane *N*-hydrochloride. R. T.

Phthaloylation of anthranilamide. Synthesis of 4-keto-1:2-o-benzoylene-1:4-dihydroquinazoline. G. B. CRIPPA and R. CARACCI (Gazzetta, 1938, 68, 109—112).—Anthranilamide and o-C₆H₄(CO)₂O at 135—160° give o-phthalimidobenzamide, m.p. 225°, also obtained from Me o-phthalimidobenzoate (new prep. from the acid and MeOH—H₂SO₄) and 33% aq. NH₃. When kept in a desiccator, (I) loses H₂O, giving 4-keto-1:2-o-benzoylene-1:4-dihydroquinazoline (II), m.p. 242°. E. W. W.



Preparation and therapeutic properties of certain acridine derivatives. II. Derivatives of s-(6-amino-2-quinolyl)-5-acridylethenes. W. L. GLEN, M. M. J. SUTHERLAND, and F. J. WILSON. Note on trypanocidal action. C. H. BROWNING, P. BROWNING, R. GULBRANSEN, and J. V. M. ROBB (J.C.S., 1938, 654—657).—6-Acetamidoquinaldine methiodide [ethiodide (I), m.p. 265—270° (decomp.)] and acridine-5-aldehyde give s-(6-acetamido-2-quinolyl methiodide)-5-acridylethene (II), m.p. 233—240° (decomp.), the methochloride, m.p. 220—228° (decomp.), of which with HCl affords s-(6-amino-2-quinolyl methochloride)-5-acridylethene hydrochloride, m.p. 205—210° (decomp.). Me₂SO₄ and (II) in PhNO₂ yield s-(6-acetamido-2-quinolyl methosulphate)-5-(acridyl methosulphate)ethene, m.p. 225—235° (decomp.), converted into the dimethochloride. A similar series of reactions with (I) gives s-(6-acetamido-2-quinolyl ethiodide)-5-acridylethene, m.p. about 238° (decomp.), s-(6-amino-2-quinolyl ethochloride)-5-acridylethene hydrochloride, m.p. 280—300° (decomp.), and s-(6-acetamido-2-quinolyl metho-p-toluenesulphonate)-5-acridylethene, m.p. about 250° (decomp.), and -5-(acridyl methosulphate)ethene, m.p. 245—248° (decomp.). 6-Dimethylaminoquinaldine methiodide and acridine-5-aldehyde yield s-(6-dimethylamino-2-quinolyl methiodide)-5-acridylethene [methochloride, m.p. 200—210° (decomp.)]. The compounds show trypanocidal action, which is discussed. F. R. S.

Synthesis of phenyl- and pyridyl-glyoxalines. G. R. CLEMO, T. HOLMES, and G. C. LEITCH (J.C.S., 1938, 753—755).— ω -Aminoacetophenone hydrochloride and KCNS give 5(4)-phenylglyoxaline-2-thiol, m.p. 267.5° (picrate, m.p. 177°), and phenacylthiocarbamide, m.p. 136°; the thiol is oxidised (HNO₃) to 5(4)-phenylglyoxaline. Et picolinoylacetate and N₂H₄ afford 5-2'-pyridylpyrazolone, m.p. 219°. 2-Acetylpyridineoxime, from Et picolinate, and p-C₆H₄Me·SO₂Cl yield O-p-toluenesulphonyl-2-acetylpyridineoxime, m.p. 81—82°, which with K followed by HCl gives 2-(ω -aminoacetyl)pyridine hydrochloride, m.p. 171—172° (decomp.). This compound and KCNS form 5(4)-2'-pyridylglyoxaline-2-thiol, m.p. 247—248° [hydrochloride, m.p. 303° (decomp.)]; picrate (+2EtOH), m.p. 194—195°, oxidised (HNO₃) to 5(4)-2'-pyridylglyoxaline, m.p. 112° (picrate, m.p. 207—208°). A similar series of reactions starting with Et nicotinate leads to O-p-toluenesulphonyl-3-acetylpyridineoxime, m.p. 78°, 3-(ω -aminoacetyl)pyridine hydro-

chloride, m.p. 172° (decomp.), 5(4)-3'-pyridylglyoxaline-2-thiol, m.p. 291—292° (hydrochloride, m.p. 241—242°), and 5(4)-3'-pyridylglyoxaline, m.p. 117—118° [dinitrate, m.p. 200° (decomp.); picrate, decomp. 285°]. F. R. S.

Quinoline derivatives. IV. T. N. GHOSH (J. Indian Chem. Soc., 1938, 15, 89—94; cf. A., 1936, 866).—Acetylcarbethoxythioacetocarbamic acid and $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ in EtOH give the Et ester (I), m.p. 128—129°, of α -2-benziminazolylacetocetic acid (II), m.p. 172° (hydrochloride, m.p. 290—291°). With NHPh-NH_2 in AcOH, either (I) or (II) gives 1-phenyl-4-(2'-benziminazolyl)-3-methylpyrazolone, m.p. 172—173° (hydrochloride, m.p. 282—284°). The anilide, m.p. 255° (decomp.), of (II) [from (I) and NH_2Ph] in conc. H_2SO_4 at 100° yields 2-hydroxy-3-(2'-benziminazolyl)-4-methylquinoline-3-sulphonic acid, m.p. 293—294° (hydrochloride). 2-Diacetylmethylbenziminazole (III) (*loc. cit.*) and NH_2Ph at 145—150° give 8-anilo- γ -2-benziminazolyl- β -pentanone, m.p. 315—316° (decomp.), which in conc. H_2SO_4 at 100° yields 3-(2'-benziminazolyl)-2:4-dimethylquinoline, m.p. 328—330° [picrate, m.p. 250° (decomp.); hydrochloride, m.p. >300°]. With $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ (III) yields 3-(2'-benziminazolyl)-2:4-dimethyl-6:7-benzo-1:5-heptadiazine, m.p. >310° (hydrochloride, m.p. >300°). E. W. W.

Syntheses in the pyrazolinoquinoline series. III. A. KOCWA (Bull. Acad. Polonaise, 1937, A, 571—578; cf. A., 1938, II, 70).—3- α -Naphthylimino-1-phenyl-5-methyl-2:3-dihydropyrazole (from the pyrazolone, α - $\text{C}_{10}\text{H}_7\text{-NH}_2$, and POCl_3 at 270°), m.p. 137—138° (hydrochloride, m.p. 183°; picrate, m.p. 169—170°), with PhNCO , PhNCS , or α - $\text{C}_{10}\text{H}_7\text{-NCO}$ at 200° gives the 4-phenylcarbamyl (I), m.p. 168°, 4-phenylthiocarbamyl, m.p. 259—260° [converted by HCl-EtOH at 140—150° into (I)], and 4- α -naphthylcarbamyl derivative, m.p. 224—225°, respectively. With PhNCO at 235—240° or $\text{C}_{10}\text{H}_7\text{-NCO}$ at 260—280°, however, 4-anilino-, m.p. 179—180° [NO-derivative, m.p. 186° (decomp.)], and 4- α -naphthylamino-7:8-benzo-1'-phenyl-5'-methylpyrazolino-3':4'-2:3-quinoline, m.p. 218—219°, are obtained; with KOH-EtOH at 200—220° both these products give 4-hydroxy-7:8-benzo-1'-phenyl-5'-methylpyrazolino-3':4'-2:3-quinoline, m.p. 235°. R. S. C.

Derivatives of 2-phenyl-3-p-(carbo- β -diethylaminoethoxy)phenyl-2:3-dihydro-1:3:4-naphthoisotriazine-6-sulphonic acid. A. NERI and (SIGNA.) G. GRIMALDI (Ann. Chim. Farm., 1938, 1, 53—60).—Na 2-p-(carbo- β -diethylaminoethoxy)-benzeneazo-1-naphthylamine-4-sulphonate with PhCHO , $\text{o-OH-C}_6\text{H}_4\text{-CHO}$, etc. gives 2-phenyl-, 2-o'-hydroxyphenyl-, 2-p'-methoxyphenyl-, 2-(4'-hydroxy-3'-methoxyphenyl)-, and 2-styryl-3-p-(carbo- β -diethylaminoethoxy)phenyl-2:3-dihydro-1:3:4-naphthoisotriazine-6-sulphonic acid. None of these has m.p. <300°. E. W. W.

New pyridine derivatives with analeptic and cardiotonic action. G. CHARRIER and M. JORIO (Ann. Chim. Farm., 1938, 1, 9—17).—3-Benzeneazo-2:6-diaminopyridine is oxidised ($\text{CuSO}_4\text{-NH}_3$) to 6-amino-8-phenyl-2:3-pyridino-7:8:9-triazole, m.p. 215° [$(\text{SO}_3\text{H})_x$ derivative, m.p. >300° (decomp.)],

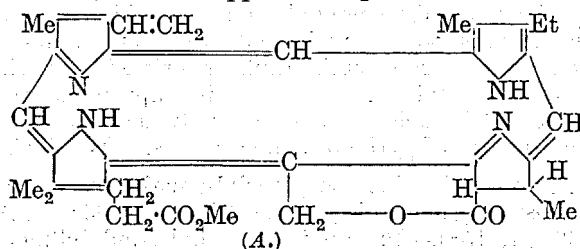
which with CH_2O and NaHSO_3 yields the 6-methylene-amino-derivative (?), m.p. 275—280°, and with $\text{CH}_2\text{Cl-CO}_2\text{H}$ gives a product, m.p. 242—243°.

E. W. W.

Purine nucleosides. VII. Guanosine and guanine deoxyriboside. J. M. GULLAND and L. F. STORY (J.C.S., 1938, 692—694).—9-Methylxanthine and POCl_3 give 2:6-dichloro-9-methylpurine, m.p. 153°, which by successive treatment with NaOH and aq. NH_3 affords 9-methylguanine (I). The spectra of 7 and 9-methylguanine are widely different in neutral and in alkaline solution, whereas those of guanosine, guanine deoxyriboside, and (I) closely resemble each other. F. R. S.

Synthesis in the alloxazine, isoalloxazine (flavin), and lumazine groups. II. Synthesis of some amino-derivatives of alloxazine and thioalloxazine. K. GANAPATHI (J. Indian Chem. Soc., 1938, 15, 77—82).—Piloty's "ureidamidoazine" (A., 1904, i, 821), from $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and violuric acid, is now regarded as 7-aminoalloxazine (I), which with CH_2N_2 gives the 2:4:7- Me_3 derivative, no m.p. <345°. The hydrochloride of 1:2:4- $\text{C}_6\text{H}_3(\text{NH}_2)_3$ (II) and alloxan condense to a product, no m.p. <350°, which is probably identical with (I). The hydrochloride of $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and thiovioluric acid give 7-amino-2-thioalloxazine, no m.p. <340°. In the prep. of (II), 2:4:1- $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-NHAc}$ (III) [new m.p. 125—126° (decomp.); improved prep. described] is hydrolysed to 2:4:1- $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-NH}_2$; when aq. KOH , followed by EtOH , is added to (III), an explosive product, m.p. ~325° (decomp.), is formed. E. W. W.

New purpurins and chlorins. H. FISCHER, K. KAHR, M. STRELL, H. WENDEROTH, and H. WALTER (Annalen, 1938, 534, 292—296).—An addendum to A., 1937, II, 470. The pyrochloran- γ -carboxy-6-lactonic ester and pyrochlorin-6-carboxy- γ -lactonic ester are identical and are chlorin e_4 - γ -hydroxymethyl-lactone (A). Its formation from chlorin e or mesochlorin is readily understood, but its formation from the ψ -chlorins appears inexplicable.



H. W.

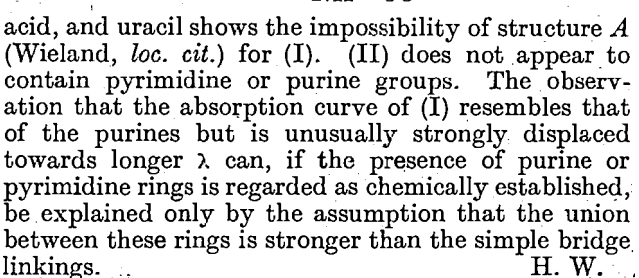
Rate of conversion of chlorophyll into phaeophytin. M. A. JOSLYN and G. MACKINNEY (J. Amer. Chem. Soc., 1938, 60, 1132—1136).—The rate of change of chlorophyll into phaeophytin by 0.05—0.0001N- H_2SO_3 , H_2SO_4 , $\text{H}_2\text{C}_2\text{O}_4$, and HCl in COMe_2 is found by visual spectrophotometry at 5350 Å. to be $\propto [\text{H}^+]$ and $\propto [\text{chlorophyll}]^n$, n being probably 2. After 40% change, however, the rate decreases except with $\text{H}_2\text{C}_2\text{O}_4$. Only phaeophytin is formed in the early stages. Chlorophyll- a is completely changed under the conditions used, whilst $-b$ is barely affected. R. S. C.

The crude product obtained by the formylation of isochloroporphyrin a_4 Me₂ ester hæmin is converted by NH₂OH in boiling C₅H₅N into *phæoporphyrin a₅ Me₂ ester oxime*, decomp. >300°, whereby dehydrogenation is caused by NH₂OH. 9-Hydroxydeoxophæoporphyrin a_5 Me₂ ester hæmin, m.p. 284° (corr.; decomp.), is described. Phyllohæmin is transformed by Na and isoamyl alcohol into mesophyllochlorin. Pyrroporphyrin Me ester Zn salt, C₃₂H₃₄O₂N₄Zn, m.p. 238° (corr.), is hydrogenated to mesopyrrochlorin Me ester.

Bacteriochlorophyll. II. H. FISCHER, R. LAMBRECHT, and H. MITTENZWEI (Z. physiol. Chem., 1938, 253, 1—39; cf. A., 1937, III, 486).—Purple bacteria occur in the shells of the pearl oyster (*Pteria vulgaris*, Schum.). A large-scale method of propagating the bacteria is described. They contain catalase but no sterols. Bacteriochlorophyll *a* (II), bacteriopheophorbide *a* (III) and its Me ester, and the Me_3 ester of bacteriopurpurin 7 (IV) are attacked by chlorophyllase (I) but the Me_3 ester of bacteriochlorin e_6 is not. The bacteria contain bacteriochlorophyllide *a* (V) [spectrum identical with that of (II)], which gives (III) when Mg is removed, and bacteriomethylchlorophyllide *a* (spectrum identical with that of bacteriochlorophyll) with CH_3N_2 . (II) is converted by (I) into a mixture of (V) and (III). *Bacteriopheophytin a* (VI) [from (II) and HCl], m.p. 204°, and bacteriomethylpheophor-

Polarographic studies of organic compounds.
—See A., 1938, I, 361.

Absorption of light by leucopterin, the wing pigment of common white butterflies. H. FROMHERZ and A. KOTZSCHMAR (Annalen, 1938, 534, 283—287).—Comparison of the absorption spectra of leucopterin (I) (Wieland *et al.*, A., 1933, 1370) and the C₁₄ compound (II) obtained therefrom (A., 1937, II, 392) with those of uric acid, guanine, barbituric



Xanthylindoles. G. ILLARI (Gazzetta, 1938, 68, 103—109; cf. A., 1937, II, 524).—Xanthhydrol reacts

$C_{19}H_{21}O_4N$, m.p. 102° , which contains 3 OMe. From *C. aurea* are isolated (I), (IV), capaurine, capauridine, corydaline, *l*-tetrahydropalmatine (V), corypalline, *dl*-tetrahydropalmatine, $C_{21}H_{25}O_4N$, m.p. 152° [identical with a product obtained by oxidising (V) with I and reduction of the palmatine iodide thus obtained with Zn and HCl], (III), *aurotensine*, $C_{19}H_{21}O_4N$, m.p. (hydrated) 128° (*hydrochloride*), also derived from *C. ochotensis* and *Fumaria officinalis*, *cordrastine* (A), m.p. 196° after darkening, (*hydrobromide*), *alkaloid F 24*, $C_{19}H_{23}O_4N$, m.p. 138° , which contains 3 OMe, *alkaloid F 27*, $C_{21}H_{23}O_4N$, m.p. 148° , which contains 4 OMe, and *alkaloid F 28*, $C_{17}H_{19}O_3N$, m.p. 135° , which contains 2 OMe.

Active principles of curare. P. DE B. CARNEIRO (Compt. rend., 1938, 206, 1202—1204).—Aq. extracts of the bark of *Strychnos lethalis*, Barb., treated by Bertrand's method (A., 1899, ii, 456) afford the silicotungstates, $C_{66}H_{81}O_{12}N_3 \cdot 12WO_3 \cdot SiO_2 \cdot 2H_2O$ and $C_{75}H_{90}O_{21}N_3 \cdot 12WO_3 \cdot SiO_2 \cdot 2H_2O$, of *lethaline*, $C_{22}H_{27}O_4N$, and *curaletaline*, $C_{25}H_{30}O_7N$, respectively.

Seeds of *Solanum xanthocarpum* (Schard and Wendle). II. M. P. GUPTA and S. DUTT (J. Indian Chem. Soc., 1938, 15, 95—100; cf. A., 1937, II, 190).—The EtOH extract of the defatted seeds, extracted with AcOH, yields the glueo-alkaloid, solanocarpine (I) (cf. A., 1937, II, 39), new formula, $C_{44}H_{74}O_{11}N_2$, new m.p. 272° , $[\alpha]_D^{20} + 83.5^\circ$ (? solvent). In the extraction of (I), the NH_3 - K_2CrO_4 method is used; the Pb salt and H_2S method (*loc. cit.*) causes hydrolysis. The *chromate* of (I) is hydrolysed (5% HCl) to *solanocarpigenine*, $C_{32}H_{54}O_2N_2$, m.p. 196° , $[\alpha]_D^{20} + 88.79^\circ$, with glucose, rhamnose, and KCl. The residue after AcOH extraction (above) yields a lactone, "*solanocarpone*," $C_{28}H_{42}O_7$, m.p. 78° (which is $\Delta^{\alpha\beta}$ -unsaturated), together with carpesterol (*loc. cit.*), $[\alpha]_D^{20} - 80^\circ$ (*Bz* derivative, m.p. 216°).

Berbine. VI. Examples and contributions from the chemistry of the alkaloids to the double linking rule of O. Schmidt. W. AVE [with H. UNGER] (Arch. Pharm., 1938, 276, 253—271).—Explanation is afforded by the double linking rule (Schmidt, A., 1935, 203 *et seq.*) of the enhanced stability of papaverine in comparison with laudanose towards oxidising agents, the carbonine-meconine fission of narcotine by heating with H_2O at 140° , by oxidation, or by reduction, and the transformations of morphine and thebaine under the influence of acids. Explanation is also afforded of the observation that 9-benzyldeoxyberberine (I) loses CH_2Ph when oxidised with $Hg(OAc)_2$ whereas the 9-Ph compound with $Hg(OAc)_2$ or I gives 9-phencylberberinium salts. In extension it is shown that (I) is converted by I in boiling EtOH followed by reduction into 16:17-dihydrodeoxyberberine. Similarly, berberinium iodide is obtained from 9-benzyldeoxy-16:17-dihydroberberine, m.p. 165° or m.p. 146° . Berberinone

and $CH_2Ph \cdot MgCl$ followed by KI afford 9-benzylberberinium iodide.

Senecio alkaloids. Alkaloids of *S. platyphyllus*. R. A. KONOVALOVA and A. P. OREKHOV (J. Gen. Chem. Russ., 1938, 8, 273—287).—Previously published results (A., 1935, 764, 1387; 1936, 1277; 1937, II, 163, 265) are given.

Constitution of matrine. XX. Oxymatrine. E. UCHIAI and Y. ITO (Ber., 1938, 71, [B], 938—942; cf. A., 1937, ii, 526).—Oxymatrine (I) has m.p. (anhyd.) 207 — 208° or $(+H_2O)$ 162 — 163° (decomp.), $[\alpha]_D^{25} + 47.7^\circ$ in EtOH; it is readily characterised as the picrate, decomp. 215 — 216° . Reduction of (I) with HI and red P yields matrine (II) and matric acid. Attempts to arylate (I) or to replace a possible OH by halogen were fruitless. When catalytically reduced it absorbs exactly 2 H. SO_2 at room temp. or acidified KI converts (I) into (II). The probability that (I) is *matrine N-oxide* is confirmed by its prep. from (II) and H_2O_2 . KOH-EtOH transforms (I) into *K oxymatrate*, decomp. 195° , whence *oxymatric acid* (III) $(+H_2O)$, decomp. 236° . (III) is not methylated but is converted into (I) by CH_2N_2 in Et_2O -MeOH. MeI and (III) in MeOH afford I and Me methylmatrate methiodide, m.p. 217 — 218° .

Ambaline, a new non-phenolic alkaloid from *Pycnarrhena manillensis*, Vidal. M. I. VILLANOS and A. C. SANTOS (Univ. Philippines Nat. Appl. Sci. Bull., 1935, 4, 338—341).—*Ambaline*, $C_{15}H_{12}O(NMe)_2$, m.p. 203 — 204° , yields a *platini-chloride*, m.p. 240° , an *aurichloride*, m.p. 170° (decomp.), and a *picrate*, m.p. 238° (decomp.). Colour reactions are described.

Binary systems containing arsenic trichloride and 5-chloro-5:10-dihydrophenarsazine. N. PUSHIN and K. S. HRUSTANOVIC (Ber., 1938, 71, [B], 798—801).—Examination of the mixed m.p. graphs shows that $AsCl_3$ and $NHPh_2$ give a *compound* (1:1), m.p. 76° , $AsCl_3$ and 5-chloro-5:10-dihydrophenarsazine (I) yield a *product*, $NH(C_6H_4)_2AsCl_3 \cdot 5AsCl_3$, stable only below 38° , $AsCl_3$ and *o*-, *m*-, and *p*- $C_6H_4Me \cdot NH_2$ give *compounds*, $AsCl_3 \cdot 3C_6H_4Me \cdot NH_2$, m.p. 140° , 162° , and 200° , respectively, whilst *m*- $C_6H_4Me \cdot NH_2$ also yields the *product*, $AsCl_3 \cdot C_6H_4Me \cdot NH_2$, stable below 97° . A compound is not formed from (I) and CH_2BzCl or $NHPh_2$.

Mercuration of diphenyl ether and some of its derivatives. W. D. SCHROEDER and R. Q. BREWSTER (J. Amer. Chem. Soc., 1938, 60, 751—753).— Ph_2O and <1 mol. of HgO in $AcOH$ - Ac_2O at 100° give the 4-*HgOAc*- (I), m.p. 150° , and 4:4'-(*HgOAc*) $_2$ - derivative, m.p. 195 — 200° . With CH_2PhCl at 100° (I) gives 4-benzyl-, b.p. 193 — $196^\circ/4$ mm., and 4:4'-dibenzyl-diphenyl ether, b.p. 260 — $270^\circ/4$ mm., which are also obtained from Ph_2O , CH_2PhCl , and 0.1 mol. of $HgCl_2$; dissociation of (I), therefore, precedes its reaction. Anhyd. $CdCl_2$ or $ZnCl_2$ is a still more efficient catalyst. With $BzCl$ or *tert*- $C_5H_{11}Cl$ at 150° (I) gives 4-benzoyl-, m.p. 66° (also obtained from Ph_2O , $BzCl$, and $HgCl_2$), and 4-*tert*-amyl-diphenyl ether, b.p. 190 — $200^\circ/23$ mm., respectively. Reactions with

inorg. reagents are normal. 4-Chloromercuri- and 4:4'-dichloromercuri-diphenyl ether have m.p. 192° and 250°, respectively. 4-Bromo-4'-acetoxy-, m.p. 152—155°, and 4'-chloro- m.p. 190°, and 4-benzoyloxy-4'-acetoxy-mercuridiphenyl ether, m.p. 165°, are also prepared. *p*-OH·C₆H₄·OPh, however, gives a mixture of polymercurated products. *p*-C₆H₄Br·OPh and 3% Na-Hg in EtOAc-PhMe at 120° give 4-mercuribis(diphenyl ether), m.p. 135—137°.

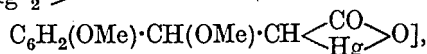
R. S. C.

Electron-sharing ability of organic radicals.
IX. Reversible splitting of organomercuric cyanides. E. CARR, I. B. JOHNS, and R. M. HIXON (J. Amer. Chem. Soc., 1938, 60, 891—894; cf. A., 1935, 1321).—The reaction, $\text{HgR}\cdot\text{CN} + \text{HCl} = \text{HgRCl} + \text{HCN}$, is reversible in EtOH at 25°, the amounts of cyanide increasing in the order, R = C₆H₁₁ (146°, 163°), Et (56.5°, 192°), CH₂Ph (127°, 103°), *o*-C₆H₄Cl·CH₃ (138°, 111°), *p*-C₆H₄Me (221°, 233°), Ph (209°, 251°), and α -C₁₀H₇ (236°, —). The figures in parentheses are the m.p. of the cyanides and chlorides, respectively.

R. S. C.

Reactivity of the double linking in coumarins and related $\alpha\beta$ -unsaturated carbonyl compounds
V. Action of mercuric acetate on cinnamic acid and its derivatives. S. RANGASWAMI, V. S. RAO, and T. R. SESHADRI (Proc. Indian Acad. Sci., 1938, 7, A, 296—303; A., 1938, II, 26).—CHPh:CH·CO₂H and Hg(OAc)₂ in MeOH give Hg^{II} cinnamate, m.p. 194° (sinters at about 160°), which in MeOH very slowly at 0°, slowly at 28°, and rapidly when heated, gives the anhydride (I), $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}\langle\text{CO}\rangle_{\text{Hg}}\text{O}$, which is stable in MeOH only if pure.

p-OMe·C₆H₄·CH:CH·CO₂H in cold MeOH gives the impure Hg salt, decomp. 161°, which very rapidly yields a product, decomp. 204°, which is partly mercurated in the ring. With 4 mols. of Hg(OAc)₂ in hot MeOH β :4-dimethoxy- α :3:5-triacetoxymercuro- β -phenylpropionic acid, decomp. 181°, is obtained, which is converted by dil. H₂SO₄ into the anhydride, SO₄''[3:5:4-Hg⁺₂ >



decomp. 223°, and by dil. HCl into 4-methoxy-3:5-dichloromercuricinnamic acid, decomp. 204°. In the cold *m*-NO₂·C₆H₄·CH:CH·CO₂H gives the Hg salt, decomp. 189°, but, when heated, yields the anhydride [as (I)], decomp. 214°, no mercuration of the ring occurs. In hot MeOH the *o*-NO₂-acid gives a similar anhydride, decomp. 215°, but no reaction occurs in the cold owing to the low solubility of the acid. H₂S removes the Hg and reduces the ethylenic linking of the anhydrides [type (I)] in NaOH solution. Thus are prepared β -methoxy- β -phenyl-, m.p. 97—98°, β -*p*-anisyl-, m.p. 144—145°, β -*m*-nitrophenyl-, m.p. 117—118°, and β -*o*-nitrophenyl-propionic acid, m.p. 151—152°.

R. S. C.

Mercury derivatives of the *o*-chlorobenzyl radical. F. E. WARE with R. M. HIXON (J. Amer. Chem. Soc., 1938, 60, 1262—1263).—*o*-C₆H₄Cl·CH₂·MgHal and HgHal₂ give *o*-chlorobenzylmercuri-iodide, m.p. 148°, -chloride, m.p. 111°, and -bromide, m.p. 128°. The chloride yields the acetate,

m.p. 101.5°, benzoate, m.p. about 58—59° (softens at 56°), and nitrate, m.p. 96°. An excess of HgCl₂ gives Hg di-*o*-chlorobenzyl, m.p. 101°, which with the corresponding Hg salt gives the mercuri-acetate or -halide.

R. S. C.

5:10-Dihydrophenphosphazine derivatives. P. G. SERGEEV and D. G. KUDRIASCHOV (J. Gen. Chem. Russ., 1938, 8, 266—272).—NHPh₂ and PCl₃ are heated at 200° for 6 hr., and the product is extracted with H₂O, to yield 5-hydroxy-5:10-dihydrophenphosphazine (I), shrinking, but not melting, at 215—216°. (I) and SOCl₂ yield the 5-Cl-derivative (not isolated), which with NaOEt in EtOH gives 5-ethoxy-5:10-dihydrophenphosphazine, m.p. 151.5—152°. (I) in boiling tetrahydronaphthalene is oxidised by atm. O₂ to phenphosphazinic acid,

$\text{NH}\langle\text{C}_6\text{H}_4\rangle\text{PO}\cdot\text{OH}$, not melting at 250° (Ag salt; Me ester, m.p. 112—114°; Et ester, m.p. 99°), a NO₂-derivative of which is described.

R. T.

Compounds of quinquevalent phosphorus.
Triphenyl- α -naphthylphosphonium salts. G. V. MEDOX (J. Gen. Chem. Russ., 1938, 8, 298—301).—O₂ passed through a solution in Et₂O of PPh₃, Mg, and 1-C₁₀H₇Br yields triphenyl- α -naphthylphosphonium bromide, from which the iodide, m.p. 270°, and hydride are prepared. The base yields sparingly sol. ppts. with CrO₄', MnO₄', and I'.

R. T.

Action of selenium tetrachloride on esters of salicylic acid. R. E. NELSON, E. F. DEGERING, and J. A. BILDERBACK (J. Amer. Chem. Soc., 1938, 60, 1239—1241).—Esters, *o*-OH·C₆H₄·CO₂R, condense with pure SeCl₄ at room temp. to give rather unstable chlorides, 1:2:4-OH·C₆H₃(CO₂R)·SeCl₃, readily hydrolysed, e.g., by moist air, to the stable hydroxides, which regenerate the chlorides by AcCl. Heating gives compounds, SeCl₂[C₆H₄(OH)·CO₂R-4:2:1]₂. Prolonged heating gives waxes, but, when R = Me, 4:4'-dihydroxy-3:3'-dicarbomethoxyselenobenzene, m.p. 136.1—136.6°, was obtained, and, when R = Ph, a compound, [2:1:4-CO₂·C₆H₄Cl·C₆H₃(OH)]₄Se, m.p. 97.5—90° (decomp.), is formed. 4-Hydroxy-3-carbomethoxy-, m.p. 167—168°, -carbomethoxy-, m.p. 159.1°, and -carboxy-phenylselenium trichloride, m.p. 148°, and the corresponding trihydroxides, m.p. 162.4—162.9°, 142.4°, and 115°, respectively, are described.

R. S. C.

Reaction of the Grignard reagent with silicon tetrafluoride. II. Tribenzylfluoromonosilane. G. V. MEDOX (J. Gen. Chem. Russ., 1938, 8, 291—293).—SiF₄, CH₂PhCl, and Mg in Et₂O yield tribenzylfluoromonosilane, b.p. 235.5°/7.5 mm., m.p. 79°, together with some Si(CH₂Ph)₄.

R. T.

New method of preparing silicon-organic compounds. Reaction of magnesium benzyl chloride with sodium silicofluoride. E. M. SOSCHESTVENSKAJA (J. Gen. Chem. Russ., 1938, 8, 294—297).—Na₂SiF₆ with CH₂Ph·MgCl at 160—170°, but not at room temp., gives Si(CH₂Ph)₄.

R. T.

Amphoteric properties of certain globulin fractions of normal horse serum. A. A. GREEN (J. Amer. Chem. Soc., 1938, 60, 1108—1115).—

Globulins from horse-serum are separated by repeated dialysis at p_H 6.5 and 5 and dissolution of ppts. in alkali and adjustment to p_H 5 or 6.2 into fractions P1, P2, and P3, which have isoelectric points 5.2, 6, and 5.0, acid-combining capacities 97, 98, and 87×10^{-5} mol. per g., and base-combining capacities 100, 80, and 90×10^{-5} mol. per g., respectively. The relative solubilities at the isoelectric points are $P1 > P2 > P3$. These differences are related to the nos. of characteristic groups. Titration curves from p_H 1.6 to 12.3 are reported and analysed in terms of apparent dissociation consts.

R. S. C.

Thermal decomposition of casein. I. S. JAITSCHNIKOV (J. Gen. Chem. Russ., 1938, 8, 71—75).—Total and phosphotungstic acid-precipitable N fall steadily with time when casein is heated at 125—275°. The NH_3 -N at first rises slightly, and then falls.

R. T.

Plant phosphatides. A. HEIDUSHA and W. NEUMANN (J. pr. Chem., 1938, [ii], 151, 1—16).—The phosphatides of rape oil are purified by pptn. from C_6H_6 by MeOAc and divided by Et_2O -alcohol into 100% pure kephalin and 90% pure lecithin fractions. The former fraction yields palmitic (18.21%; no other saturated acid) and unsaturated acids (67.57%; oleic 25—28, α -44.83 and β -linoleic 11, linolenic acid 0%), colamine (92% of the total N), and glycerophosphoric acid. The latter fraction yields the same products in about the same yields, except that choline replaces the colamine. The glycerophosphoric acid is 90% the α -form, whence it is inferred that only α -kephalin and α -lecithin are present in the phosphatide, the β -forms being produced during isolation. Sugars are absent. The bitter taste is best removed by MeOAc.

R. S. C.

Determination of carbon and hydrogen. Compact, movable, and easily built combustion train. S. NATELSON and E. B. CONNER (Ind. Eng. Chem. [Anal.], 1938, 10, 276—279).—An apparatus for determining C and H on 50—125-mg. samples is described.

J. L. D.

Oven constructed by the Refractory Materials Institute, for determination of carbon and sulphur by combustion. F. K. GERKE (Zavod. Lab., 1938, 7, 236—237).—An oven is described.

R. T.

[Microanalytical determination of oxygen in organic compounds]. J. LINDNER (Ber., 1938, 71, [B], 1382).—A comment on the publication of Unterzaucher *et al.* (A., 1938, II, 209).

H. W.

Micro-tests for elements in organic compounds. C. L. WILSON (Analyst, 1938, 63, 332—335).—Middleton's method (A., 1935, 639) is adapted for tests on the micro-scale. If the test for N by glucose— Na_2CO_3 fusion fails, it is repeated with addition of Zn dust. Tests for S and halogens are described.

E. C. S.

Determination of chlorine in volatile organic compounds. S. ARUTJUNJAN and K. MIRZACHANJAN (Sintet Kautschuk, 1936, No. 1, 31—33).—The org. compound (CCl_4 , $CHCl_3$, etc.) is mixed with C_2H_2 and burned in a special burner (U.S. Bur. Stand.,

Circ. 48, 1916). The HCl formed is absorbed by 5% KOH. Cl in solution is determined with $AgNO_3$.
CH. ABS. (e)

Bromo-iodometric determination of ammonia and its application to the determination of nitrogen after destruction by Kjeldahl's method.—See A., 1938, I, 369.

Application of dielectric constant measurements to the control of distillation of organic mixtures. V. B. EVSTIGNEEV (Zavod. Lab., 1938, 7, 226—229).—The composition of distillates may in many cases be evaluated on the basis of ϵ measurements.

R. T.

Sealed-tube oxidations in qualitative organic chemistry. E. L. BROWN, N. CAMPBELL, and G. S. LEARMONTH (J. Chem. Educ., 1938, 15, 217—219).—For identification of a compound, side-chain oxidation is accomplished by heating 0.5 g. with 5 c.c. of HNO_3 (d 1.2) in a sealed hard-glass tube enclosed in a Fe tube. The products are identified by their m.p. and neutralisation equivs. The table given shows that the method is applicable to a wide range of compounds, especially in those cases when $KMnO_4$ oxidation is unsatisfactory.

L. S. T.

Micro-determination of the saponification value. M. FURTER (Helv. Chim. Acta, 1938, 21, 601—613).—Apparatus and technique for determining within $\pm 5\%$ the equiv. wt. of esters, using 5—33 mg. is described. Amides cannot be used.

R. S. C.

Detection and recognition of alcohols. W. MEYER (Chem.-Ztg., 1938, 62, 376).—The alcohol with CS_2 and KOH yields the K alkylxanthate, which, when titrated with I, is quantitatively oxidised to dixanthate. The "I val." gives the mol. wt of the alcohol; isomerides with the same I val. are recognised by the m.p. of the xanthate.

J. D. R.

Determination of acetone, *n*-butyl alcohol, and ethyl alcohol present together. II. Salting-out method. N. D. JERUSALIMSKI and M. N. BECHTEREVA (J. Appl. Chem. Russ., 1938, 11, 539—545; cf. A., 1937, II, 477).—The $COMe_2 + Bu^oOH + EtOH$ concn. is brought to 8.5—15 g. per 100 ml. by rectification of the solutions saturated with NaCl, or by dilution, and the solution is shaken with excess of K_2CO_3 in a special 30-ml. flask with a graduated neck. The vol. of the solvent layer separating is then read.

R. T.

New reaction for detection of glycerol. Possibility of colorimetric determination. M. E. POZZI-ESCOT (Bull. Assoc. Chim. Sucr., 1938, 55, 353—354).— V_2O_5 readily oxidises glycerol (I) to $AcCHO$ which may then be tested for by the known methods, e.g., by the action of phloroglucinol— H_2SO_4 mixture. The recommended procedure is described. The colour developed might serve for the colorimetric determination of (I). The reaction is sp. only in absence of other polyhydric alcohols and of OH-acids, e.g., citric acid.

I. A. P.

Identification of glyceryl trinitrate in alcoholic solution. H. CARON and D. RAQUET (J. Pharm. Chim., 1938, [viii], 27, 533—534).—Glyceryl tri-

nitrate is detected in presence of glycerol and HNO_3 by hydrolysing and testing for nitrite. A. LI.

Determination of formic acid. J. D. REID and H. D. WEIHE (Ind. Eng. Chem. [Anal.], 1938, 10, 271—272).—Boiling aq. HCO_2H is oxidised quantitatively with $\text{Hg}(\text{OAc})_2$ to CO_2 which is absorbed in NaOH and determined titrimetrically (cf. Weihe and Jacobs, B., 1936, 305). J. L. D.

Detection and determination of volatile fatty acids. II. isoButyric acid. L. KLINC (Biochem. Z., 1938, 296, 202—209; cf. A., 1934, 1331; 1937, II, 477).— $\text{Pr}^{\beta}\text{CO}_2\text{H}$ in COMe_2 (≤ 0.01 mg. in 1—5 c.c.) is detected by oxidation with KMnO_4 (H_2O_2 is less suitable), the product being pptd. with an alkaline solution of $\text{Hg}(\text{CN})_2$ and AgNO_3 . AcOH , EtCO_2H , and lactic acid do not interfere. If there is a ppt. when H_2O_2 is used but only an opalescence when KMnO_4 is used $\text{Pr}^{\alpha}\text{CO}_2\text{H}$ is present and the solution must be diluted until H_2O_2 produces only a turbidity before oxidising with KMnO_4 . For the determination of $\text{Pr}^{\alpha}\text{CO}_2\text{H}$ the liquid containing the ppt. is distilled with H_2O_2 or KMnO_4 and the COMe_2 in the distillate is determined iodometrically. $\text{Pr}^{\alpha}\text{CO}_2\text{H}$ is detected in presence of very large excess of $\text{Pr}^{\beta}\text{CO}_2\text{H}$ by evaporating to dryness and destroying $\text{Pr}^{\beta}\text{CO}_2\text{H}$ with conc. H_2SO_4 at 200° for 1 hr. For the determination of $\text{Pr}^{\alpha}\text{CO}_2\text{H}$ and $\text{Pr}^{\beta}\text{CO}_2\text{H}$ when present together (in presence or absence of other volatile fatty acids) the total acid is determined iodometrically after oxidation with H_2O_2 and the $\text{Pr}^{\beta}\text{CO}_2\text{H}$ after oxidation with KMnO_4 , the $\text{Pr}^{\alpha}\text{CO}_2\text{H}$ content being obtained by difference. W. MCC.

Colour reaction of oxalic acid. M. PAGET and R. BERGER (J. Pharm. Chim., 1938, [viii], 27, 577—579).—Aq. $\text{H}_2\text{C}_2\text{O}_4$ is reduced $[\text{Zn}-\text{HCl}]$ to $\text{CHO}-\text{CO}_2\text{H}$, which with $\text{NHPh-NH}_2\text{HCl}$ and $\text{K}_3\text{Fe}(\text{CN})_6$ yields a red colour. The reaction, which is not affected by other org. or inorg. acids, or by Na, K, Ca, Li, and NH_4 , is sensitive to 10 p.p.m.

J. D. R.

Specificity of the salicylaldehyde reaction of Csonka-Straub. T. THOMSON (Nature, 1938, 141, 917; cf. A., 1937, II, 440).—A positive reaction is not confined to compounds containing Ac linked directly to H or C. Positive results have been obtained with COEt_2 , EtCHO , cyclohexanone, and methylcyclohexanone. The colours obtained in the test are yellow only for dil. solutions; more conc. solutions give varying depths of red changing through orange to golden-yellow on dilution. The mechanism of the colour reaction involves condensation of the salicylaldehyde with a CH_2 in the α -position to an unsaturated group such as CO , and the formation of a simple alkali salt of the resulting compound. Positive results have been obtained with a 3% solution of $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ in which the CH_2 is activated by the $\text{C}\equiv\text{N}$. Fluorene gives a negative result. The enolisation mechanism suggested by Braunstein (*loc. cit.*) is untenable.

L. S. T.

Organic analysis. G. H. CHEESMAN (J. Chem. Educ., 1938, 15, 92).—A test for the presence of

esters, a method for the saponification of esters in presence of hydrocarbons, and the separation of alcohols from mixtures with esters, hydrocarbons, etc. are described. L. S. T.

Selective determination of alanine and serine + aspartic acid. C. FROMAGEOT and P. HEITZ (Mikrochim. Acta, 1938, 3, 52—67).—Kendall and Friedemann's method for the determination of alanine (I) (A., 1931, 246) has been modified to make it selective for (I). The NH_2 -acids are converted into the corresponding OH-acids by the above method, and the formation of MeCHO from the acids corresponding with serine (II) and aspartic acid (III) by oxidation with KMnO_4 is prevented by addition of $\text{Hg}(\text{OAc})_2$ solution. The MeCHO then formed represents the (I) present, and is determined colorimetrically by means of Na nitroprusside and piperazine. 2 mg. of (I) can thus be determined with an accuracy of approx. 5%. The MeCHO corresponding with (I) + (II) + (III) is found by oxidation of the corresponding OH acids with KMnO_4 , omitting the addition of $\text{Hg}(\text{OAc})_2$, and increasing the $[\text{MnSO}_4]$. The method gives 95—97% of the (I) content and 93—95% of the (II) + (III) content. Details of procedure and typical data are given. L. S. T.

Spectrographic identification and determination of small quantities of benzene. Application to the determination of benzene in an atmosphere. P. LAURIAN (J. Pharm. Chim., 1938, [viii], 27, 561—576).— C_6H_6 in EtOH solution is identified (limit 0.1 mg.) by the ultra-violet absorption spectrum, and determined by the evaluation of the optical density of the maxima (limit 2 mg. with an accuracy of 5%). C_6H_6 in the atm. is collected by condensation in 95% EtOH cooled with COMe_2 -solid CO_2 , and determined as above. J. D. R.

Determination of α - and β -carotene by means of the spectrophotometer and the photo-electric photometer. C. L. SHREWSBURY, H. R. KRAYBILL, and R. B. WITHEROW (Ind. Eng. Chem. [Anal.], 1938, 10, 253—256).—The details of the determination in *n*-heptane are described. J. L. D.

Chromatographic analysis of small amounts of carotenoids. Carotenoids of milk and serum.—See A., 1938, III, 633.

Colorimetric determination of nicotinamide. P. KARRER and H. KELLER (Helv. Chim. Acta, 1938, 21, 463—469).—Nicotinic acid and its amide, in absence of other $\text{C}_5\text{H}_5\text{N}$ derivatives, are determined colorimetrically by means of 1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ (cf. Vilter *et al.*, A., 1938, III, 496). R. S. C.

Sources of error in determination of tyrosine and tryptophan.—See A., 1938, III, 546.

Determination of small quantities of quinine and cinchonidine by absorption spectra. C. G. VAN ARKEL (Pharm. Weekblad, 1938, 75, 485—490).—Small amounts of quinine and cinchonidine (to 150 mg. per l.) in 0.1N- H_2SO_4 can be determined to within 3—5% by measuring the extinction coeff. at $\lambda = 3135$ and 3400, respectively. S. C.

A., II.—Organic Chemistry

AUGUST, 1938.

Restricted internal rotation in hydrocarbons. K. S. PITZER and J. D. KEMP (J. Amer. Chem. Soc., 1938, 60, 1515—1516).—The statement of Kistiakowsky and Wilson (cf. A., 1938, I, 178) that the authors' selection of potential barriers is arbitrary is refuted. The only assumption is that the restriction of rotation about a given C-C linking depends on the position and character of the attached groups. Uncertainties in the method depend on the accuracy of the experimental data. For C_3H_8 agreement is good.

R. S. C.

Applications of infra-red absorption spectra [in organic chemistry]. J. LECOMTE and P. LAMBERT (Publ. sci. tech. Min. de l'Air, 1933, No. 34, 1—134; Chem. Zentr., 1936, ii, 454).—A comprehensive review of work on hydrocarbons.

H. N. R.

Decomposition reactions of organic compounds in the gaseous state. C. N. HINSHELWOOD (Nature, 1938, 141, 1010—1011).—Some of the conclusions of Travers *et al.* are criticised.

L. S. T.

Induced liquid-phase decomposition of hydrocarbons. P. L. CRAMER (J. Amer. Chem. Soc., 1938, 60, 1406—1410).—Et, prepared *in situ* by decomp. of $PbEt_4$ at 200—300°, has no effect on $C_{10}H_8$ or liquid C_6H_6 . The amounts of H_2 , C_2H_4 , C_2H_6 , C_4H_{10} , and olefines obtained similarly from $n-C_7H_{16}$, Pr^iBu^r , Bu^iBu^r , $n-C_{10}H_{22}$, cyclohexane, Δ^s -hexene, $CH_2:CMcPr^i$, Pr^i , $CH_2:CHBu^r$, Δ^s -heptene, $CH_2:CMcBu^r$, $(CH_2:CMcCH_2)_2$, cyclohexene, tetra- and deca-hydronaphthalene are determined. CH_4 and products derived therefrom are not formed. Reaction is of two kinds: (a) $Et + RH \rightarrow R + C_2H_6$; (b) $Et + CHR:CH_2 \rightarrow CH_2EtR:CH_2$. Unused Et reacts thus: $2Et \rightarrow H_2 + 2C_2H_4$; $2Et \rightarrow C_2H_4 + C_2H_6$; or $2Et \rightarrow C_4H_{10}$. Saturated compounds react only by (a). Both reactions occur with olefines, (b) being favoured by mobility of H and thus by presence of many $>CH_2$ and still more so by $\geq CH$; the nature and position of the ethylenic linking, as evidenced by its reactivity, have, however, also a great effect. The results are co-ordinated with the stability, ease of oxidation, and knocking characteristics of the hydrocarbons.

R. S. C.

Probable structures of polymerides of lower olefines. A. WACHTER (Ind. Eng. Chem., 1938, 30, 822—826).—Working rules are developed for predicting the polymerisation products of simple olefines based on the position of the double linking and the probability of rearrangements. Good agreement is found with experimental results given in the literature.

E. G. H.

Addition of hydrochloric acid to unsaturated hydrocarbons at low temperature. J. J. LEENDERTSE (Rec. trav. chim., 1938, 57, 795—797).—Olefines, $\cdot CH:C(C\leq)_2$, add HCl at -78° to give $\cdot CH_2\cdot CCl(C\leq)_2$, the Cl being readily lost at higher temp. Olefines, $\cdot CH:CH\cdot$, react with HCl at -78° only in presence of $AlCl_3$ and much polymerised chloride is formed. The polymeride is not formed by $AlCl_3$ or HCl alone. No experimental details are given.

R. S. C.

Ethylenic isomerism. Δ^s -Hexene. H. VAN RISSEGHEM (Bull. Soc. chim. Belg., 1938, 47, 194—215, 221—240, 261—286).—Divinyl glycol, obtained by the action of Zn—Cu on acetaldehyde, has b.p. 97.0—97.5°/13 mm., and appears to be a mixture of isomerides. It is hydrogenated (PtO_2 in Et_2O) to hexane- $\gamma\delta$ -diol, form A (I), b.p. 102.6°/14.5 mm., m.p. 90.1—90.2°, and variety B (II), b.p. 108.65—108.75°/24 mm., m.p. 20.9°. By analogy with the m.p. of the erythritols (I) is regarded as the *meso*- and (II) as the *r-r* form. This view is confirmed by the behaviour of *B. xylinum* or *Mycoderma aceti*, which convert (I) into a dextrorotatory ketol and (II) into a levorotatory ketol with a residue of levorotatory glycol. The polymorphism of (II) is established. By-products of the hydrogenation are hexan- γ -ol, b.p. 134—136°/750 mm., characterised by oxidation to $COEtPr^s$ (semicarbazone, m.p. 111.8°), and γ -hydroxy- δ -keto-hexane, b.p. 165—169°/750 mm. (phenylosazone, m.p. 159—159.5°; semicarbazone, m.p. 140.4—141.2°), oxidised by H_2O_2 in presence of $FeSO_4$ to $EtCO_2H$. Attempts to prepare the two diastereoisomeric hexane- $\gamma\delta$ -diols from the corresponding divinyl glycols gave results less satisfactory than those just recorded. Hydrogenation (Pt -black in Et_2O) of $(\cdot COEt)_2$ slowly yields (I) without appreciable formation of (II) with unchanged initial material. The principal product of the action of depolymerised glyoxal on $MgEtBr$ is (II) but (I) is formed in small amount.

The action of PBr_3 in $CHCl_3$ on (II) in the same solvent gives $\gamma\delta$ -dibromohexane (III), b.p. 81.0—81.2°/15 mm., and γ -bromohexane, b.p. 49—49.2°/26 mm., converted by $KOH-CH_2Ph\cdot OH$ into a mixture of Δ^s - and Δ^r -hexene, 67.75—68.25°/760 mm. The formation of HBr , H_3PO_3 , PH_3 , PH_4I , and P_4H_2 is observed. The changes involved are probably: $H_3PO_3 + 3PBr_3 = 3POBr_3 + PH_3$ and $2H_3PO_3 + 6PBr_3 = 6POBr_3 + P_2H_4 + H_2$. The action of PBr_3 on a mixture of (I) and (II) leads to a dibromohexane (IV), b.p. 79.2—83.2°/15.5 mm. Granulated Zn and (III) in boiling $EtOH$ afford Δ^r -hexene, b.p. 67.28—67.35°/760 mm., whereas the corresponding dibromide from (I) gives a hexene, b.p. 66.50—66.72°/760 mm.,

and (IV) gives mainly *cis*- Δ^7 -hexene, b.p. 66.58—66.93°/760 mm., possibly containing a little of the *trans* derivative. Addition of Br in CHCl_3 to the hexene from any source yields a $\gamma\delta$ -dibromohexane b.p. 82.5°/16 mm., transformed by NaOPh in boiling EtOH into γ -bromo- Δ^7 -hexene, b.p. 34°/16 mm., which adds Br in CHCl_3 giving $\gamma\gamma\delta$ -tribromohexane, b.p. 118.6—119.0°/18 mm. This is converted by NaOEt in EtOH into $\gamma\delta$ -dibromo- Δ^7 -hexene, b.p. 72.2—74.2°/19 mm., which with Zn in boiling EtOH affords Δ^7 -hexinene, b.p. 81.65—81.98°/760 mm., which does not react with AgNO_3 -EtOH or with CaCl-NH_3 but gives a white ppt. with HgCl in $\text{H}_2\text{O-EtOH}$; its Raman spectrum contains a line 2245 Å. not observed previously in an analogous aliphatic hydrocarbon. Semi-hydrogenation (Raney Ni or Bourguet Pd) gives pure *cis*- Δ^7 -hexene, b.p. 66.85—67.15°/760 mm.

H. W.

Proof of the constitution of cetene. N. SCHOORL (Rec. trav. chim., 1938, 57, 719—726).—The difference in $[R]$ due to the terminal ethylenic linking in the pairs, $(\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)_2\text{-}n\text{-C}_8\text{H}_{14}$, Δ^7 -pentenoic-valeric acid, $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{H}$ -undecic acid (I), and Δ^8 -octene-octane, is -0.50 to -0.57 (average -0.54). That for the non-terminal linking in the pairs, Δ^6 -hexene-hexane, Δ^8 -octene-octane, Δ^8 and Δ^7 -hexenoic-hexic, elaidic-stearic acid, $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$ (I), is -0.07 to -0.15 (average -0.10). The best val. for the difference for cetene and $n\text{-C}_{16}\text{H}_{34}$ is -0.52, conclusively proving that cetene is $\Delta^8\text{-C}_{16}\text{H}_{32}$.

R. S. C.

Criterion for the mechanism of reaction between alkyl halides and hydroxylic solvents. Reactions of *tert*-butyl chloride. L. C. BATEMAN, E. D. HUGHES, and C. K. INGOLD (J.C.S., 1938, 881—887; cf. A., 1935, 452).—A means is recorded of distinguishing between the two mechanisms of nucleophilic aliphatic substitution, one involving replacement in a single stage, the other, preliminary ionic fission. In bimol. substitution, the product is determined in a reaction the rate of which can be measured, whilst in unimol., it is formed, not in the rate-measured process, but in a subsequent fast reaction. Rate measurements of simultaneous hydrolysis and alcoholysis of Bu^tCl , and a determination of the amounts of EtOBu^t or MeOBu^t , Bu^tOH (by difference), and *isobutylene* (by standard bromometric method), indicate that the reaction is unimol., confirming Hughes (*loc. cit.*). If the reaction were bimol. (cf. Olson and Halford, A., 1938, I, 86), the rate-derived consts. would allow calculation of the composition of the substitution product (alcohol + ether). There is no interconversion of products once formed. A summary is given of the four main methods (and their limitations) available for the diagnosis of reaction mechanism in those first-order substitutions in which the direct kinetic method is unavailable.

A. T. P.

Syntheses of polychloro-compounds by aluminium chloride. V. Condensation of hexachloropropylene with trichloroethylene. H. J. PRINS (Rec. trav. chim., 1938, 57, 659—666; cf. A., 1937, II, 438).— $\text{CCl}_3\cdot\text{CCl}:\text{CCl}_2$ (I), C_2HCl_3 , and AlCl_3 in CH_2Cl_2 or CHCl_3 at 35—37° give $\alpha\alpha\beta\gamma\delta\epsilon\epsilon$ -nonachloro- Δ^8 -pentene (II), b.p. 128°/2—3 mm., and

two $\alpha\alpha\beta\gamma\delta\epsilon\epsilon$ -octachloro- $\gamma\text{-}\alpha'\beta'\beta'\text{-tetrachloroethyl-}\Delta^8$ -pentenes, m.p. 58—62° and 94—96°, respectively, the formation of the C_7 compounds being favoured by use of an excess of C_2HCl_3 . The same products are isolated as by-products of the interaction of CCl_4 with C_2HCl_3 , owing their formation to decomp. of the primary product, $s\text{-C}_3\text{HCl}_7$, to (I). At higher reaction temp. (II) loses HCl to give the known octachloropentadienes, which are at once isomerised by the AlCl_3 to the known octachlorocyclopentene; these products are obtained from pure (II) by the successive action of KOH-EtOH and AlCl_3 , and incidentally establish the structure of (II). $\pm 95\text{--}96\%$ H_2SO_4 at 75—80° converts (II) into a difficultly separable mixture of hexachloropentenoic acids, e.g., the $\alpha\beta\gamma\delta\delta\delta$ -hexachloro- Δ^8 -acid (acids, m.p. 132—134° and 75—81°, were isolated), which with KOH-EtOH give difficultly separable pentachloropentadienoic acids (acids, m.p. 61—66° and 120.5—122.5°, were isolated), converted by Cl_2 in light into (?) heptachloropentenoic acid.

R. S. C.

Synthesis and pharmacological action of some $\beta\beta\beta$ -trialkylethanol. R. V. RICE, G. L. JENKINS, and W. C. HARDEN (J. Amer. Pharm. Assoc., 1938, 27, 303—305).—The prep. (Grignard) of the (β) Me_3 b.p. 111—113°, m.p. 49°, Me_2Et , b.p. 134—135°, MeEt_2 , b.p. 150—151°, and Et_3 derivative, b.p. 76—77°/11 mm., of EtOH is described. All possess anaesthetic properties but to a smaller extent than does $\text{CBr}_3\cdot\text{CH}_2\cdot\text{OH}$.

F. O. H.

Constants of ethylene glycol and propylene glycol. A. G. PUKIREV (Sborn. Rabot Lab. Inst., 1937, 15, 45—50).— $(\text{CH}_2\cdot\text{OH})_2$ was synthesised from $(\text{CH}_2\text{Br})_2$ and KOH and propylene glycol by the method of Wurtz (Ann. Chim. Phys., 1859, 55, 438). The b.p., n , and d are recorded.

D. G.

Preparation of a *d*-mannitol dibromohydrin tetra-acetate. H. VOGEL (Ber., 1938, 71, [B], 1272).—Prolonged treatment of mannitol hexaacetate with saturated HBr-AcOH at room temp. give a *d*-mannitol dibromohydrin tetra-acetate, m.p. 201° (corr.), $[\alpha]_D^{20} +10.26^\circ$ in CHCl_3 .

H. W.

Behaviour of glycerol mono- and di-triphenylmethyl ethers towards Criegee's reagent. P. E. VERKADE (Rec. trav. Chim., 1938, 57, 824—828).—The structures assigned to glycerol α - and β - CPh_3 ether are confirmed by the much faster reaction of the α - than of the β -ether with Pb(OAc)_4 in C_6H_6 ; in AcOH the difference is much less, probably owing to hydrolysis. In no case does reaction cease with use of 1 mol. of reagent. The difference in rate of reaction of the $\alpha\alpha'$ - and $\alpha\beta$ - $(\text{CPh}_3)_2$ ethers in $\text{AcOH-C}_6\text{H}_6$ is too small to be significant.

R. S. C.

Interaction of *l*- β -octyl nitrite and *dl*- β -butanol. J. KENYON and D. P. YOUNG (J.C.S., 1938, 965—966).—*l*- β -Octyl nitrite (1 mol.), b.p. 63—65°/15 mm., $\alpha_{441} -5.28^\circ$, and *dl*- β -butanol (I) (2 mols.) afford *dl*- β -Bu nitrite, some *l*- β -octanol, and unchanged (I). The mechanism of interaction of a nitrous ester and an alcohol ("The Organic Chemistry of Nitrogen," Sidgwick, 1937) is not proved.

A. T. P.

Mercaptols. A. SPORZYŃSKI (Arch. Chemji Farm., 1936, 3, 59—66; Chem. Zentr., 1936, ii, 1704).—

EtSH and HCl in COMe_2 afford Et mercaptol, b.p. 69–70°/11 mm.; decomp. of this at 125° and distillation at 140–200° yields EtSH and Et isopropenyl sulphide. Bu^a mercaptol, b.p. 112–112.5°/5.5 mm., (I) obtained similarly, yields BuSH and Bu isopropenyl sulphide (II) [in presence of ZnCl_2 (II) is further decomposed into BuSH and an unsaturated hydrocarbon] and oxidation with KMnO_4 yields dimethyldibutyl sulphone, m.p. 67.8–68°. An additive compound of (I) with HgCl_2 , m.p. 172° (decomp.), is described. A. H. C.

Interaction of chlorine with different types of organic sulphur compounds. I. B. DOUGLASS and T. B. JOHNSON (J. Amer. Chem. Soc., 1938, 60, 1486–1489).—Passing Cl_2 into a suspension of EtSH or $n\text{-C}_5\text{H}_{11}\text{SH}$ in H_2O at 10° gives >70% of ethyl- and *n*-amyl-sulphonyl chloride, b.p. 77–78°/3 mm., respectively. PhSH gives successively Ph_2S_2 , PhSCl (fairly stable to H_2O at 10°), and PhSO_2Cl (55%). CH_2PhSH , CH_2PhSAc , or $\text{CH}_2\text{PhNaS}_2\text{O}_3$ gives $(\text{CH}_2\text{PhS})_2$, $\text{CH}_2\text{PhSO}_2\text{Cl}$ (I), and $\text{CH}_2\text{PhSO}_2\text{S}\cdot\text{CH}_2\text{Ph}$, m.p. 108° [gives (I) when chlorinated, and is thus an intermediate product]. Bu^aS_2 gives $\text{Bu}^a\text{SO}_2\text{Cl}$, contaminated with some material substituted in the Bu; Bu^aSCl is probably an intermediate. $n\text{-C}_5\text{H}_{11}\text{SCl}$ in CCl_4 is converted by Cl_2 mainly into a product containing 3 Cl. EtSAc gives 71% of EtSO_2Cl . CH_2PhSBz gives BzCl , $\text{CH}_2\text{PhSO}_2\text{Cl}$, and a little BzOH . NaMeS_2O_3 and NaEtS_2O_3 , prepared from R_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ in H_2O or aq. COMe_2 or from RI and $\text{Na}_2\text{S}_2\text{O}_3$ in aq. COMe_2 , with $\text{H}_2\text{O}-\text{Cl}_2$ give about 55% of MeSO_2Cl and EtSO_2Cl , respectively. cycloHexyl thiosulphate could not be prepared. $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ reacts with $\text{Na}_2\text{S}_2\text{O}_3$, but the product gives no sulphonyl chloride when chlorinated. $\text{OEt}\cdot\text{CS}_2$ gives EtSO_2Cl and ClCO_2Et . *S*-Benzyl ethylxanthate, b.p. 143°/3 mm., gives ClCO_2Et , $\text{CH}_2\text{PhSO}_2\text{Cl}$, and (?) CH_2PhCl . $\text{OEt}\cdot\text{CS}_2\text{K}$ gives ClCO_2Et (33%). $\text{NBz}\cdot\text{CS}_2\text{Et}$ gives $\text{NBz}\cdot\text{CCl}_2$ and EtSO_2Cl , identified by conversion by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ into ethylsulphonyl-*p*-toluidide, m.p. 81°, and benzoyldi-*p*-tolylguanidine monohydrochloride, m.p. 193–194°, respectively. R. S. C.

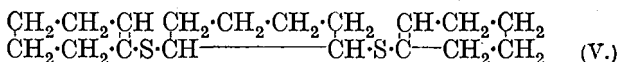
Rates of formation of six- and seven-membered ring compounds from ω -chloro-sulphides. G. M. BENNETT and (Miss) E. G. TURNER (J.C.S., 1938, 813–815).—Formation of cyclic sulphonium salts from Et ϵ -chloroamyl (I), b.p. 122°/25 mm.

$\{[\text{Et}\cdot\text{S}(\text{CH}_2)_5]_2\text{PtCl}_6\}$, and Et ζ -chlorohexyl (II), b.p. 128–131°/26 mm. $\{[\text{Et}\cdot\text{S}(\text{CH}_2)_6]_2\text{PtCl}_6\}$, sulphides, in aq. COMe_2 , is smooth and of the first order, and the 6-membered ring is formed 75 times as fast as the 7-membered (cf. ratio for 5- and 6-rings, A., 1930, 61). The reactions appear to proceed to completion, but the possibility that they are incomplete and reversible is not ignored. $\text{OH}\cdot[\text{CH}_2]_6\cdot\text{OH}$ and HCl in petroleum (cf. A., 1931, 1032) give the chlorohydrin, b.p. 116–117°/19 mm., which with $\text{KSET}\cdot\text{EtOH}$ gives $\text{OH}\cdot[\text{CH}_2]_6\cdot\text{SET}$, b.p. 134–136°/17 mm., converted by $\text{SO}_2\text{Cl}\cdot\text{CCl}_4\cdot\text{NPhEt}_2$ into (II). ϵ -Chloroamyl acetate and aq. $\text{KSET}\cdot\text{EtOH}$ afford $\text{OH}\cdot[\text{CH}_2]_6\cdot\text{SET}$, b.p. 135°/20 mm., converted into (I). Cyclisation of $\text{Cl}\cdot[\text{CH}_2]_6\cdot\text{SPh}$ is not effected in boiling 70% aq. COMe_2 , 10% aq. AcOH , or $(\text{CH}_2\cdot\text{OH})_2$. A. T. P.

Lignin. X. Reaction of sulphuric acid with unsaturated compounds. H. FRIESE (Ber., 1938, 71, [B], 1303–1306).—Conc. H_2SO_4 is added gradually to a solution of allyl alcohol in $\text{Ac}_2\text{O}\cdot\text{AcOH}$ at 0° and the mixture is heated at 60–70°, whereby $\alpha\beta$ -dihydroxypropane- γ -sulphonic acid, isolated as the Ba salt, is obtained; it is remarkably stable towards dil. H_2SO_4 and $\text{Ba}(\text{OH})_2$. Similarly $\text{CHMe}\cdot\text{CMe}_2$ affords (?) β -hydroxy- β -methylbutane- γ -sulphonic acid (Ba salt) in excellent yield. Glucal triacetate yields a tetrahydroxysulphonic acid [salt $(\text{C}_6\text{H}_{11}\text{O}_8\text{S})_2\text{Ba}$], which exists as a syrup freely sol. in H_2O but very readily resinified and then insol. This property and its powerful reducing action towards Fehling's solution indicate that SO_3H has become added at $\text{C}_{(2)}$ and the original arrangement of the glucose configuration has been restored at $\text{C}_{(2)}$. The results considered from the viewpoint of lignin do not indicate an aromatic nature of the latter. H. W.

Reaction between sulphur dioxide and olefines.

VII. Co-polymerides from mixtures of olefines, acetylenes, and olefine derivatives with sulphur dioxide. C. S. MARVEL, S. J. DAVIS, and F. J. GLAVIS (J. Amer. Chem. Soc., 1938, 60, 1450–1455; cf. A., 1937, II, 315).— SO_2 and mixed olefines, e.g., $\text{CH}_2\cdot\text{CMe}_2$ and cyclohexene (I), $\text{CH}_2\cdot\text{CHPr}^a$ (II) and $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{Me}$ (III), $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CH}_2\cdot\text{OH}$, or $\text{CPh}\cdot\text{CH}$, are polymerised by ascaridole and EtOH at room temp. The analyses, solubilities, and m.p. indicate that the products are not mixtures, but contain each olefine, even if one of them was used in preponderatingly large amount. That from 1 : 1 mol. mixtures of (II) and (III) is mainly $[\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{Me}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CHPr}^a\cdot\text{SO}_2]_n$, since liquid NH_3 gives >75% of 2-*n*-propyl-6-*o*-carboxy-*n*-octyl-1 : 4-dithian 1 : 4-bisdioxide (IV), m.p. 198°, as sole product. 5 : 1 mol. mixtures of (II) and (III) give a mixed product of the type $[\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CHR}'\cdot\text{SO}_2]_n$, since liquid NH_3 gives both (IV) and 2 : 6-di-*n*-propyl-1 : 4-dithian 1 : 4-bisdioxide. cycloHexenopolysulphone and liquid NH_3 give anomalously the product (V), m.p. 145–145.5°, converted by hot AcOH into the expected



2 : 3 : 5 : 6-bistetramethylene-1 : 4-dithian 1 : 4-bisdioxide, m.p. 291°, and (I) (not isolated). When (I) is treated with S_2Cl_2 at 55° and then with Na_2S in dry EtOH, 1 : 2-bis-1- Δ^1 -cyclohexenylthiolcyclohexane, b.p. 175–180°/16 mm., is anomalously obtained; with H_2O_2 this yields (V). The structure of the mixed product from (I) and $\text{CH}_2\cdot\text{CMe}_2$ was not determined; the product is reconverted into (I) and $\text{CH}_2\cdot\text{CMe}_2$ by alkali, and with liquid NH_3 gives a substance containing 2 SO_2 and 3 (I) units. R. S. C.

Action of sulphuric acid on aliphatic carboxylic acids of high mol. wt. and their glycerides. J. HERZER (Seifens.-Ztg., 1936, 63, 242–243; Chem. Zentr., 1936, ii, 557).—A review. H. N. R.

Preparation of volatile acid chlorides. H. C. BROWN (J. Amer. Chem. Soc., 1938, 60, 1325–1328).—Twelve aliphatic acid chlorides are best prepared, usually in >75% yield, by distilling a mixture of the

acid and 1.5—2 mols. of BzCl. The reaction mechanism is discussed. R. S. C.

Allylic transposition. IX. A. KIRRMANN (Bull. Soc. chim., 1938, [v], 5, 915—919; cf. A., 1937, II, 175; 1938, II, 215).—The structures $\text{CH}_2\text{:CH}\cdot\text{CHCl}\cdot\text{OAc}$ (I) and $\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{CH}\cdot\text{OAc}$ (II) ascribed to compounds described previously are supported by their Raman spectra, which are analogous to those of $\text{CH}_2\text{:CH}\cdot\text{CH}(\text{OAc})_2$ and $\text{CH}_2\text{:CH}\cdot\text{CHCl}_2$ and to that of $\text{CHMe}\cdot\text{CH}\cdot\text{OAc}$, respectively. The frequency at 1417 cm^{-1} , characteristic of the vinyl group, is shown by (I) but not by (II). The CO frequency is higher in these compounds than in EtOAc. The Raman spectrum of $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{OAc})_2$ (III) contains the vinyl and C:C frequencies at 1430 and 1679 cm^{-1} , respectively. The product (b.p. $64^\circ/13\text{ mm.}$) obtained by the action of HCl on (III) is $\text{CHMeCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{OAc}$, by analogy with (II), since the mol. refraction is abnormally high, and the C-Cl frequency is at 635 cm^{-1} . The structure is confirmed by the action of Br followed by oxidation. The allylic rearrangement of $\text{CHMe}\cdot\text{CH}\cdot\text{CHCl}\cdot\text{OAc}$ to yield (III) is much more rapid than that of (I) to form (II). J. W. S.

Electrolysis of mixtures of isobutyrate with nitrates. F. FICHTER and P. SUTTER (Helv. Chim. Acta, 1938, 21, 891—900; cf. A., 1937, II, 45; 1938, II, 40).—Electrolysis of solutions $4N$ in $\text{Pr}^\beta\text{CO}_2\text{Na}$ and $2N$ in NaNO_3 , and containing 10% of Na_2CO_3 , at Pt electrodes, yields Pr^βOH , COMe_2 , $\text{Pr}^\beta\text{O}\cdot\text{NO}$, $\text{Pr}^\beta\text{NO}_3$, $\text{Pr}^\beta\text{CO}_2\text{Pr}^\beta$, $\alpha\beta\text{-C}_6\text{H}_6(\text{NO}_3)_2$, $\text{CHMePr}^\beta\cdot\text{CH}_2\cdot\text{OH}$, $\text{CHMeBu}^\beta\cdot\text{OH}$, COMeBu^β , and $\beta\gamma\text{-C}_6\text{H}_{12}(\text{OH})_2$. The theory of the reactions involved is discussed. J. W. S.

Transformations of esters of unsaturated fatty acids with hydrogenation catalysts in the absence of hydrogen. H. I. WATERMAN and C. VAN VLODOP (Rec. trav. chim., 1938, 57, 629—636).—Et oleate is shown by change in the van der Ster I equilibrium const. (Diss., Delft, 1928) to be converted into Et elaidate by heating with 10% of Ni-kieselguhr in N_2 at 290° . This change also occurs, but much more slowly, when the oil is heated alone or with 10% of kieselguhr. R. S. C.

Configuration of optical antipodes of various substances. J. TIMMERMANS (Rec. trav. chim., 1938, 57, 525—528).—The relationship of (–)- $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}_2$, (+)- $\text{CHMeBr}\cdot\text{CO}_2\text{H}$ (I), (–)-malic, (+)-aspartic, (+)-lactic, (–)-tartaric acid, (–)- $(\text{CHCl}\cdot\text{CO}_2\text{H})_2$, and (+)-asparagine, deduced by the author's method, agrees with that of Kuhn and Freudenberg, except for (I). R. S. C.

Optical rotation of *d*-lactic acid and its derivatives. I. Anhydride formation of muscle-lactic acid at ordinary temperatures. II. Benzoylation of *d*-lactic acid. S. FUKUDA (J. Biochem. Japan, 1938, 27, 241—246, 247—249).—I. Tabulated data are given for $[\alpha]$ of H_2O -*d*-lactic acid (I)—lactic anhydride (II) mixtures of $[\alpha]$ $+2.40^\circ$ [H_2O 10.65; (I) 89.35, (II) 0%] to $[\alpha]$ -64.21° [H_2O approx. 2.35, (I) 2.76, (II) 99.59%]. (I) is considered to be partly in the hydrated form in the more dil. solutions. II. (I) with BzCl at 110° yields α -benzoyloxypropionic

acid (III), m.p. 84° , $[\alpha]_D^{20} +15.91^\circ$ in EtOH, $+44.31^\circ$ in C_6H_6 . Vals. for $[\alpha]$ of the oily mixture of (III) and its anhydride are compared with those of Strecker (1854) and Wislicenus (1865). F. O. H.

α -Hydroxyacetoacetic acid. I. Preparation, properties and estimation. H. WEIL-MALHERBE (Biochem. J., 1938, 32, 1033—1044).—Solutions of α -hydroxyacetoacetic acid (I) (containing AcOH) are obtained by hydrolysis of Et α -acetoxyacetate in presence of NaOH under anaërobic conditions at 25° . (I) loses CO_2 relatively slowly at p_H 7.4, but much more rapidly at low p_H vals. and especially in presence of NH_2Ph ; this reaction carried out at p_H 4.6 may be conveniently applied for manometric determination. The acid is oxidised by mol. O_2 in $0.1M\text{-NaHCO}_3$, 1 mol. of O_2 being absorbed and 1 mol. each of CO_2 , AcOH, and EtHC_2O_4 formed, and also in $0.1N\text{-NaOH}$ with the formation of 1 mol. each of CO_2 , HCO_2H , and AcOH, the last apparently in a polymerised form. W. O. K.

Action of hydrobromic acid on $\beta\zeta$ -epoxyheptane- γ -carboxylic [2 : 6-dimethyltetrahydropyran-3-carboxylic] acid. Δ^4 -Hepten- β -ol. M. DELÉPINE (Rec. trav. chim., 1938, 57, 520—524).—2 : 6-Dimethyltetrahydropyran-3-carboxylic acid, m.p. 91° , and 40% HBr-AcOH at 100° give impure $\beta\zeta$ -dibromoheptane- γ -carboxylic acid, an oil, which with Na_2CO_3 gives ζ -bromo- Δ^4 -heptene (I), b.p. $114\text{—}116^\circ/164\text{ mm}$ (by way of

$\text{O} \begin{array}{c} \text{CMe} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CH}\cdot[\text{CH}_2]_2\cdot\text{CHMeBr}$), and the lactone, b.p. $141\text{—}143^\circ/23\text{ mm.}$, of ζ -hydroxy- Δ^4 -heptene- γ -carboxylic acid (by way of $\text{CHMe} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{CO} \end{array} \text{CH}\cdot\text{CHMeBr}$). With $\text{AgOAc}\cdot\text{AcOH}$ (I) gives ζ -acetoxy- Δ^4 -heptene, b.p. $127\text{—}129/170\text{ mm.}$, hydrolysed by $\text{KOH}\cdot\text{EtOH}$ to Δ^4 -hepten- ζ -ol, b.p. $160\text{—}161^\circ$ (diphenylurethane, m.p. 96°). R. S. C.

Diene syntheses. XXX. Acetylenedicarboxyl chloride. O. DIELS and W. E. THIELE (Ber., 1938, 71, [B], 1173—1178).— $(\text{C}\cdot\text{CO}_2\text{H})_2$ is converted by PCl_5 in AcCl into chlorofumaryl chloride, b.p. $66\text{—}68^\circ/13\text{ mm.}$ Treatment of anthracene-9 : 10-endo-acetylenedicarboxylic anhydride with PCl_5 at 115° in a sealed tube gives unchanged anhydride, anthracene-9 : 10-endoacetylenedicarboxyl chloride (I), m.p. 112° , and anthracene-9 : 10-endodichloromaleic anhydride, m.p. 235° , also obtained from dichloromaleic anhydride. (I) is converted by MeOH into Me_2 anthracene-9 : 10-endoacetylenedicarboxylate, m.p. 161° , and by $\text{NH}_3\cdot\text{H}_2\text{O}$ in Et_2O into anthracene-9 : 10-endoacetylenedicarboxylamide, m.p. 285° , whence (P_2O_5 in boiling MeCN) the corresponding dinitrile, m.p. 263° . The temp. of decomp. of (I) is so high that the reaction products are anthracene, CO, CO_2 , and COCl_2 ; at lower temp. (I) distils almost entirely unchanged. When heated at $185\text{—}195^\circ$ with maleic anhydride (I) yields acetylenedicarboxyl chloride (II), m.p. 115° , and Me_2 fumarate whilst (II) and (?) chloropropiolyl chloride, b.p. $77.5^\circ/9\text{ mm.}$, are isolated from the product obtained at $205\text{—}210^\circ$. (II) is very sensitive to moisture. It is characterised by conversion into the corresponding Me_2 ester and thence into Me_2 pyrazole-4 : 5-dicarboxylate, m.p. 141° . H. W.

Oxidation of sorbic acid and, particularly, of its methyl ester with molecular and peroxidic oxygen. P. HEINÄNEN (Ann. Acad. Sci. Fennicæ, 1938, [A], 49, 7—112; cf. A., 1935, 731).—Autoxidation of Me sorbate (I) yields Me H fumarate (II), Me fumaraldehyde, AcOH, MeCHO, and a polymerised peroxide, $(C_7H_{10}O_4)_4$. Autoxidation of (I) is examined under varying conditions of concn., solvent, acidity, light (Hg quartz lamp), and in presence of catalysts, e.g., Os, $PdCl_2$, $FeCl_3$. (I) and H_2O_2 -MeOH give a peroxide, $(C_7H_{10}O_4)_5$. (I) and BzO_2H in $CHCl_3$ give Me $\gamma\delta$ -oxido- Δ^a -hexenoate (III), b.p. $89^\circ/10$ mm. [hexenoic acid, m.p. 84 — 86° (Ag salt)], which with $KMnO_4$ -NaOH affords $\alpha\beta$ -oxido-butyric acid and with H_2O_2 gives (II). (III) and NaOH form $\gamma\delta$ -dihydroxy- Δ^a -hexenoic acid, m.p. 68 — 77° (Ag salt). Ozonisation of (I) in $CHCl_3$ forms a mixture of mono- and di-ozonides.

A. T. P.

Isomeric α - β -methylmalic [α -hydroxy- β -methylsuccinic] acids. E. B. ABBOT and A. MCKENZIE (Ber., 1938, 71, [B], 1214—1217).— $COEt \cdot CO \cdot CHMe \cdot CO_2Et$ is reduced by Al-Hg in Et_2O better than by Na-Hg to $Et_2 \alpha$ -hydroxy- β -methylsuccinate (I), b.p. $116^\circ/11.5$ mm., hydrolysis of which gives α -hydroxy- β -methylsuccinic acid A, m.p. 122 — 123° , also obtained in modest yield by condensation of $CHMe(CO_2Et)_2$ with $CCl_3 \cdot CHO$ in presence of C_5H_5N ; it is partly resolved into its optical antipodes by quinine in H_2O . With well-cooled NH_3 -MeOH (I) yields a mixture of r - α -hydroxy- β -methylsuccindiamide A (II), m.p. 159 — 160° (decomp.), and B (III), m.p. 203° (decomp.). Alkaline hydrolysis of (II) appears to give a mixture of acids whereas that of (III) leads to r - α -hydroxy- β -methylsuccinic acid B, m.p. 124 — 125° ; this can be partly resolved by brucine.

H. W.

Optical activation of racemic acid by (+)-citramalic acid. E. B. ABBOT, E. A. KIDNEY, and A. MCKENZIE (Ber., 1938, 71, [B], 1210—1213).—(+)-Citramalic [α -hydroxy- α -methylsuccinic] acid (I), m.p. 108 — 109° , $[\alpha]_D^{25} +23.2^\circ$, $[\alpha]_{589}^{25} +27.7^\circ$ in H_2O , is obtained by resolution of the r -acid by brucine in H_2O . Addition of 1 mol. of (I) to an aq. solution of r -tartaric acid neutralised with KOH causes the separation of a feebly dextrorotatory mixture of K H r -tartrate (II) and K H (+)-tartrate. A similar mixture is obtained by crystallisation of (II) from an aq. solution of (I).

H. W.

Oxidation of l -ascorbic acid in presence of ammonia or primary amines. J. PARROD (Bull. Soc. chim., 1938, [v], 5, 938—941).— l -Ascorbic acid and aq. NH_3 , NH_2Me , or N_2H_4 afford $(CO \cdot NH_2)_2$, $(CO \cdot NHMe)_2$, and $(CO \cdot NH \cdot NH_2)_2$, respectively. NH_2Et , NH_2Bu^a , NH_2Bu^s , $NH_2 \cdot [CH_2]_2 \cdot CHMe_2$, and $NH_2 \cdot C_6H_{11}$ similarly give the corresponding di-substituted NN -oxamides (cf. A., 1936, 968).

A. T. P.

Biochemistry of carbohydrates. XXX. Iodometric determination of glycuronic acid. Y. TANABE (J. Biochem. Japan, 1938, 27, 251—256).—The sample [equiv. to 2—8 mg. of glycuronic acid (I)] is hydrolysed with conc. HCl and the hydrolysate is neutralised and steam-distilled, the solution

being maintained just saturated with NaCl. The distillate is treated with 0.01N-NaHSO₃ followed by 0.01N-I, excess of which is titrated with 0.01N-Na₂S₂O₃ [1 c.c. = 0.48 mg. of furfuraldehyde (II) or 3.36 mg. of (I)]. Chondrosin ester gives < theoretical yields of (II).

F. O. H.

Glycuronic acid as intermediate in biochemical formation of citric acid from sugar.—See A., 1938, III, 696.

Essential oil of *Achasma Wolang*, Val. P. VAN ROMBURGH (Rec. trav. chim., 1938, 57, 494—499).—The oil from the leaves (0.25%), stems (0.21%), and roots (0.15%) of this plant contains n - Δ^a -decenaldehyde (I), b.p. 229 — $231^\circ/760$ mm., $104^\circ/13$ mm. [semicarbazone, m.p. 162° ; no colour with $C(NO_2)_4$], with smaller amounts of n - Δ^a -octenaldehyde, b.p. $83^\circ/14$ mm. [semicarbazone, m.p. 163° ; oxidised by O_2 to n - Δ^a -octenoic acid, b.p. 245° (Ag salt), and by $KMnO_4$ to n -hexoic acid], a terpene, b.p. 165° , $[\alpha] -22^\circ$, and Δ^a -dodecenaldehyde (oxidised by O_2 to Δ^a -dodecenoic acid and by $KMnO_4$ to $\alpha\beta$ -dihydroxy-lauric acid). With O_2 (I) gives n - Δ^a -decenoic acid (II), b.p. $165^\circ/15$ mm., m.p. 8° (Ag salt; chloride, b.p. 120 — $122^\circ/14$ mm.; amide, m.p. 121°), with $KMnO_4$ gives n - $C_7H_{15} \cdot CO_2H$, with H_2 -Pt-black gives n -decanol, and with H_2 -PtO₂ gives n - $C_9H_{19} \cdot ClO$ or, by oxidation, n -decoic acid. The root oil contained 30% of (II), probably formed during storage.

R. S. C.

Preparation of *dl*-erythro- $\alpha\beta$ -dihydroxy-butanaldehyde. J. W. E. GLATTFELD and W. G. STRATTEFF (J. Amer. Chem. Soc., 1938, 60, 1384—1387).— $OH \cdot CHMe \cdot CH(OH) \cdot CO_2H$ (OH are *cis*), now termed *dl*-erythro- $\alpha\beta$ -dihydroxybutyric acid (prep. from *trans*- $CHMe \cdot CH \cdot CO_2H$ and BzO_2H modified to give an 80% yield), m.p. 81.5° (open tube), 82.5° (closed tube) [$NHPh \cdot NH_2$ salt, m.p. 105.5° (decomp.)]; phenylhydrazide, m.p. 123.5° ; Me, b.p. $109^\circ/10$ mm., Et, b.p. $113^\circ/10$ mm., *Pr*^a, b.p. $117^\circ/10$ mm., *Bu*^a, b.p. $127^\circ/10$ mm., and *n*-amyl ester, b.p. $139^\circ/10$ mm., with Ac_2O -HCl gives the diacetate, $+2H_2O$, m.p. 50° , and anhyd., an oil, b.p. about 127° (decomp.)/ 4 mm., converted by $SOCl_2$ into the acid chloride diacetate, b.p. $79^\circ/3$ mm., which is hydrogenated (Pd - $BaSO_4$) in xylene at 150° to *dl*-erythro- $\alpha\beta$ -diacetoxypentaldehyde, b.p. $87^\circ/4$ mm., in 87.3% yield. 0.1N-HCl yields the (OH)₂-aldehyde, an oil, the osazone, m.p. 173° , from which was obtained by Wohl and Frank (A., 1902, i, 532) from "methylglyceraldehyde."

R. S. C.

Ketones from higher fatty acids. VII—IX. K. KINO (J. Soc. Chem. Ind. Japan, 1938, 41, 91—94b; cf. A., 1937, II, 483).—Ketone formation from fatty acids and MnO, $MnCO_3$, and $MgCO_3$ at $\sim 330^\circ$ for 0.5, 1, and 1.5 hr. is studied. Intermediate soap formation must be as rapid as possible to prevent frothing. MnO and $MnCO_3$ cause frothing, also induced by $MgCO_3$ unless in excess, but MgO and certain proportions of Mg-MgO, Mg- $MgCO_3$, and $MgCO_3$ -MgO give no frothing.

A. T. P.

Transformation of dihydroxyacetone derivatives into pyruvaldehyde derivatives. C. L. BERNIER and W. L. EVANS (J. Amer. Chem. Soc.,

1938, 60, 1381—1384).—*Dihydroxyacetone monoacetate semicarbazone*, m.p. 137.5—138°, and *m-nitrobenzoylhydrazine*, decomp. 253—260°, are converted, when recrystallised or heated with 16% H_3PO_4 , into *pyruvaldehyde-disemicarbazone*, m.p. 265—267° (decomp.), and *m-nitrobenzoylosazone*, m.p. 278—282° (decomp.) (both also obtained from AcCO_2H), respectively, with liberation of $\text{CO}(\text{CH}_2\cdot\text{OH})_2$ and AcOH .

R. S. C.

Preparation of diisopropylidene-sugars. H. VAN GRUNENBERG, C. BREDT, and W. FREUDENBERG (J. Amer. Chem. Soc., 1938, 60, 1507).—By adding fused ZnCl_2 (120) and P_2O_5 -85% H_3PO_4 (20 : 40) successively to the sugar (100 g.) in COMe_2 (2 l.) and stirring at room temp. for 2 hr., pure diisopropylidene derivatives are obtained in the yields stated from the following sugars: *l*-sorbose 85, *d*-arabinose 90, *d*-galactose 78, *d*-mannose 92, and *d*-glucose 75%. The products are those normally obtained by use of H_2SO_4 .

R. S. C.

Application of cyclic acetals. G. SLOOFF (Rec. trav. chim., 1938, 57, 673—676).—The use of cyclic acetals for purifying sugar alcohols, determining orientation of diols, and protecting CO etc. during reactions is stressed *o*- $\text{C}_6\text{H}_4\cdot\text{O}_2\text{CMe}_2$ and HNO_3 (*d* 1.2—1.4) give (quant.) 4-nitro- and 4 : 5-dinitro-pyrocatechol, and thence readily the 4- NH_2 - (I) and 4 : 5-(NH_2)₂-compounds. The isopropylidene derivative of (I), but not (I) itself, is readily diazotised and gives the usual diazo-reactions.

R. S. C.

Inter-conversion of simple sugars. (Sir) J. C. IRVINE and G. J. ROBERTSON (Rec. trav. chim., 1938, 57, 575—581).—Recorded reactions and conversion of galactose into an idose derivative (unpublished) indicate that conversion of a simple sugar into another is effected artificially only by way of derivatives containing an ethylene oxide ring.

R. S. C.

Carbonate derivatives of the sugars. W. N. HAWORTH, C. R. PORTER, and A. C. WAINE (Rec. trav. chim., 1938, 57, 541—547).—Passing COCl_2 into galactose in COMe_2 gives diisopropylidenegalactose 6-chloroformate (I), m.p. 53°, $[\alpha]_{\text{D}}^{25}$ —56° in 33% aq. COMe_2 , also obtained from diisopropylidenegalactose by COCl_2 in PhMe and hydrolysed thereinto by $\text{Ba}(\text{OH})_2$ in aq. EtOH. With NH_2Ph in Et_2O (I) gives diisopropylidenegalactose-6-phenylcarbimide, m.p. 84—85°, $[\alpha]_{\text{D}}^{25}$ —49° in EtOH, with MeOH at room temp. gives 6-carbomethoxydiisopropylidenegalactose, m.p. 94°, $[\alpha]_{\text{D}}^{25}$ —49° in EtOH (decomposed by hot H_2O), and with 12*N*-HCl-MeOH gives 6-carbomethoxy- α -methylgalactopyranoside, decomp. 141°, $[\alpha]_{\text{D}}^{25}$ +150° in H_2O , converted by $\text{Ba}(\text{OH})_2$ into α -methylgalactoside and BaCO_3 . Xylose and COCl_2 in COMe_2 give 1 : 2-isopropylidenexylose 3 : 5-carbonate, m.p. 138°, $[\alpha]_{\text{D}}^{25}$ +7.5° in CHCl_3 , +19.5° in COMe_2 , +9° in MeOH (hydrolyses, when kept), converted in MeOH or MeOH-HCl into 5-carbomethoxy-1 : 2-isopropylidenexylose (II), m.p. 135—136°, $[\alpha]_{\text{D}}^{25}$ —13° in MeOH, also obtained from isopropylidenexylose (III) and ClCO_2Me in NaOH-aq. MeOH. (II) gives the 3-*p*-toluenesulphonate, m.p. 106°, $[\alpha]_{\text{D}}^{25}$ —14° in MeOH, hydrolysed by $\text{Ba}(\text{OH})_2$ to 1 : 2-isopropylidenexylose 3-*p*-toluenesulphonate, m.p. 64—66°, $[\alpha]_{\text{D}}^{25}$ —15° in MeOH; the 5-*p*-toluenesulphonate, m.p. 138—139°,

is obtained from (III). Mannose dicarbonate (IV) and SOCl_2 in dioxan give α -chloromannose dicarbonate, m.p. 192° (sinters at 186°), $[\alpha]_{\text{D}}^{25}$ +67° in COMe_2 , converted by MeOH- Ag_2CO_3 -dioxan into β -methylmannofuranoside dicarbonate, m.p. 219—220°, $[\alpha]_{\text{D}}^{25}$ —89° in COMe_2 . β -Ethylmannofuranoside dicarbonate, m.p. 153—156°, $[\alpha]_{\text{D}}^{25}$ —74° in COMe_2 , is similarly prepared. Aq. Br- BaCO_3 converts (IV) into the acid, which yields *Me mannonate dicarbonate*, m.p. 200—202° (decomp.).

R. S. C.

2 : 6-Dimethylglucose. D. J. BELL and R. L. M. SYNGE (J.C.S., 1938, 833—836; cf. A., 1937, II, 484).—4 : 6-Ethylidene- β -methylglucoside 2 : 3-dinitrate and NaI in COMe_2 at 100° afford the 3-nitrate (I), m.p. 146—148°, $[\alpha]_{\text{D}}^{25}$ —30.8° in CHCl_3 . The 2-*Me* derivative of (I), m.p. 104.5—105.5° after softening at 101°, $[\alpha]_{\text{D}}^{25}$ —28.7° in CHCl_3 , and $\text{Na}_2\text{S}\cdot\text{EtOH}$ give 4 : 6-ethylidene-2-methyl- β -methylglucoside, m.p. 122—123°, also obtained from 2-methyl- β -methylglucoside and paraldehyde (H_2SO_4) at 0°. (I) and $\text{Ac}_2\text{O}\cdot\text{H}_2\text{SO}_4$ give 2 : 6-diacetyl-4- α -acetoxethyl- β -methylglucoside 3-nitrate, m.p. 125—126° after softening at 124°, $[\alpha]_{\text{D}}^{25}$ +13.4° in CHCl_3 , converted by HNO_3 (*d* 1.5) in CHCl_3 into 2 : 6-diacetyl- β -methylglucoside 3 : 4-dinitrate, m.p. 90—91°, $[\alpha]_{\text{D}}^{25}$ —27.3° in CHCl_3 , which with NaOMe- CHCl_3 at room temp. forms β -methylglucoside 3 : 4-dinitrate, m.p. 116—118°, $[\alpha]_{\text{D}}^{25}$ +13.9° in MeOH. 2 : 6-Dimethyl- β -methylglucoside 3 : 4-dinitrate, m.p. 74—76°, $[\alpha]_{\text{D}}^{25}$ —13.7° in CHCl_3 , and NaOH-EtOH- H_2S at 100° give 2 : 6-dimethyl- β -methylglucoside, m.p. 50—52°, $[\alpha]_{\text{D}}^{25}$ —43.5° in CHCl_3 (3 : 4-di-*p*-toluenesulphonate, m.p. 156—158°, $[\alpha]_{\text{D}}^{25}$ —8.2° in CHCl_3) (cf. A., 1932, 500), converted by dil. HCl at 100° into 2 : 6-dimethylglucose (not cryst.), $[\alpha]_{\text{D}}^{25}$ +58.3° in H_2O (2 : 6-dimethylgluconophenylhydrazide, m.p. 127—129°, $[\alpha]_{\text{D}}^{25}$ +48.6° in EtOH).

A. T. P.

β -Methylglucoside 2 : 3 : 6-trinitrate. D. J. BELL and R. L. M. SYNGE (J.C.S., 1938, 836—838; cf. preceding abstract).— β -Methylglucoside 2 : 3-dinitrate and $\text{CPh}_3\text{Cl}\cdot\text{C}_5\text{H}_5\text{N}$ at 37° afford the 6- CPh_3 ether, which with $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ at room temp. gives 4-acetyl-6-triphenylmethyl- β -methylglucoside 2 : 3-dinitrate, m.p. 153—155°, $[\alpha]_{\text{D}}^{25}$ +31.8° (rotations in CHCl_3), converted by HNO_3 (*d* 1.5) in CHCl_3 at 0° into 4-acetyl- β -methylglucoside 2 : 3 : 6-trinitrate, m.p. 94—95°, $[\alpha]_{\text{D}}^{25}$ +0.4°. NaOMe- CHCl_3 then gives β -methylglucoside 2 : 3 : 6-trinitrate (not cryst.). Its constitution is proved by methylation ($\text{Ag}_2\text{O}\cdot\text{MeI}$) to the 4-*Me* derivative, removal of nitrate ($\text{AcOH}\cdot\text{Zn}\cdot\text{Fe}$) followed by acetylation (Ac_2O) yielding 4-methyl- β -methylglucoside 2 : 3 : 6-triacetate, m.p. 105—106°, $[\alpha]_{\text{D}}^{25}$ —34.9°.

A. T. P.

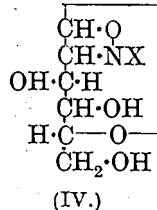
New ethylidene compounds of α - and β -methylglucosides. H. APPEL and W. N. HAWORTH [with, in part, E. G. Cox and F. J. LLEWELLYN] (J.C.S., 1938, 793—797).— α - and β -Methylglucoside and paraldehyde (H_2SO_4) form 2 : 3-oxidoethylidene-4 : 6-ethylidene- α - (I), m.p. 182.5—183.5°, $[\alpha]_{\text{D}}^{25}$ +83.5° in CHCl_3 , and - β - (II), m.p. 208—209°, $[\alpha]_{\text{D}}^{25}$ —57.8° in CHCl_3 , -methylglucosides, confirmed by MeCHO and mol. wt. determinations. The structure of 4 : 6-ethylidene- α -methylglucoside (III), $[\alpha]_{\text{D}}^{25}$ +109.1° in H_2O , is confirmed (cf. Hibbert and Hill, A., 1924, i,

133); (III) and MeI-Ag₂O in COMe₂, followed by PhCHO-ZnCl₂, yield 4 : 6-benzylidene-2 : 3-dimethyl- α -methylglucoside, $[\alpha]_D^{25} +96.2^\circ$ in CHCl₃. (I) or (II) and Et₂O-Br yield (III) and the β -glucoside, new m.p. 189—190°, $[\alpha]_D^{19} -76.9^\circ$ in H₂O, respectively, suggesting that 2 mols. of MeCHO are involved in linking between C₁₂ and C₁₃ of the glucose chain. 4 : 6-Benzylidene- α -methylglucoside affords a 2 : 3-*oxido-diethylidene* derivative, m.p. 192—193°, $[\alpha]_D^{20} +66.4^\circ$ in CHCl₃, similar in configuration and structure to (I). X-Ray data are recorded and the bearing of the results on configuration is discussed.

A. T. P.

Halogenoalkyl glucosides. III. Quaternary salts. Glucosamine quaternary derivative.

H. W. COLES and F. H. BERGEM (J. Amer. Chem. Soc., 1938, 60, 1376—1379; cf. A., 1938, II, 261).—The prep. of tetra-acetyl- β -D-glucosido-1-trimethylammonium bromide (I), m.p. 192°, $[\alpha]_D^{18} +10.2^\circ$ in H₂O, is improved; it yields the Ac-free salt (II), m.p. 161—162°, $[\alpha]_D^{18} +5^\circ$. β -D- β -Bromoethylglucoside tetra-acetate and NEt₃ in C₆H₆ give tetra-acetyl- β -D-glucosidoethyltriethylammonium bromide, m.p. 67°, $[\alpha]_D^{20} -33^\circ$ in H₂O. β -D-Glucosidocholine chloride (III) (prep. in aq. EtOH), a syrup, and Ac₂O at 100° give the tetra-acetate, m.p. 217—218°, $[\alpha]_D^{20} -25^\circ$ in H₂O, also obtained from β -D- β -chloroethylglucoside tetra-acetate and NEt₃ in C₆H₆ at 100°. β -D- γ -Chloropropylglucoside tetra-acetate gives γ -tetra-acetyl- β -D-glucosidohomocholine chloride, m.p. 165—167.5°. Glucosamine hydrochloride and MeI in hot KOH-MeOH give the substance (IV) (X = Me₂I, 2MeI), m.p. >280°, which gives no picrate and reacts with Fehling's solution only in presence of acid. (I), (II), and (III) have no effect on the blood-pressure of rabbits in doses of 5 mg. per kg. body-wt. (IV) has an action similar to that of choline; 1 mg. per kg. produces slight spasms and marked vagal stimulation, followed by 180% increase in blood-pressure (returning to normal in 2 min.) if stimulation is abolished by atropine. M.p. are corr. R. S. C.



wt. (IV) has an action similar to that of choline; 1 mg. per kg. produces slight spasms and marked vagal stimulation, followed by 180% increase in blood-pressure (returning to normal in 2 min.) if stimulation is abolished by atropine. M.p. are corr. R. S. C.

Lotaustralin and its Ac derivative, m.p. 127—128.5°. See A., 1938, III, 633.

Amino-alcohols. I. Preparation and dehydration of certain aliphatic tertiary amino-alcohols. B. K. CAMPBELL and K. N. CAMPBELL (J. Amer. Chem. Soc., 1938, 60, 1372—1376).—In accordance with expectation from the inductive effect, the ease of dehydration of *tert.* alcohols is greatly decreased and that of esterification increased by the proximity of a basic group to the OH, the influence being dependent on the distance separating these groups. Addition of CH₂Cl-CO₂Me to MgMeI gives CH₂Cl-CMe₂-OH, converted by NHMe₂ in C₆H₆ at 135—140° into dimethylaminotert.-butyl alcohol (I), b.p. 130—130.3°/743 mm. (hydrochloride, m.p. 114.5—115.5°; aurichloride, m.p. 126—128°), which readily gives a benzoate hydrochloride, m.p. 200°, resists heating with anhyd. CuSO₄ or KOH, and is only partly converted by I into a substance, m.p. 113° (contains ionisable I). With MgEtBr (I) gives a complex, decomposed at 280° into α -dimethylamino- Δ^{α} -isobutene (II), the structure of which follows from the

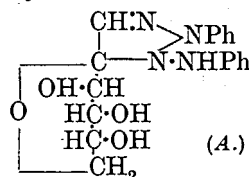
L* (A., II.)

hydrolysis of its unstable hydrochloride, m.p. 142—150°, by dil. HCl to Pr ^{β} CHO and NHMe₂. With conc. H₂SO₄ at 100° (I) gives NHMe₂, Pr ^{β} CHO [probably by way of (II)], and γ -dimethylamino- Δ^{α} -isobutene (hydrochloride, m.p. 142—144°; aurichloride, m.p. 116—118°; with O₃ gives CH₂O).

CH₂Br-CH₂-CO₂Me and MgMeCl give the bromohydrin, converted by NHMe₂-C₆H₆ at 140—150° into γ -dimethylaminotert.-amyl alcohol, b.p. 160.1—160.5°/743 mm. (hydrochloride, m.p. 141—141.5°), which readily gives a benzoate hydrochloride, m.p. 165—166°, and is largely unchanged by I or KOH, but is dehydrated by CuSO₄; pyrolysis of the complex obtained with MgEtBr gives a tar. Cl-[CH₂]₃-CO₂Me (prep. in 80% yield from Cl-[CH₂]₃-CN) gives similarly ϵ -dimethylamino- β -methylpentan- β -ol, b.p. 99°/30 mm. (hygroscopic hydrochloride, m.p. 153—154°), which gives less vigorously a benzoate hydrochloride, m.p. 114°, and is unchanged by I or KOH, but is dehydrated by CuSO₄. Br-[CH₂]₄-CO₂Me gives ζ -dimethylamino- β -methylhexan- β -ol, b.p. 118—118.5°/30 mm. (hygroscopic hydrochloride, m.p. 100—101°), which gives no benzoate and is dehydrated by I. R. S. C.

Osazones. III. Dehydro-osazones. O.

DIELS, E. CLUSS, H. J. STEPHAN, and R. KÖNIG (Ber., 1938, 71, [B], 1189—1196).—Osazones of mono- and di-saccharides are readily dehydrogenated by atm. O₂ in alkaline solution to compounds very similar to the osazones but containing 2 H less. The assumption of a simple transition of osazone into the corresponding osotetrazine is negated by the impossibility of the reverse change and can scarcely be reconciled with colour and m.p. The formation of a $\cdot\text{N}\cdot\text{NPh}$ residue is also improbable. It appears most likely that dehydro-osotetrazines are first produced and become isomerised to the much more stable osotriazoles (cf. A). Thus d-glucosazone affords d-dehydroglucosazone, C₁₈H₂₀O₄N₄, m.p. 203° (triacetate, m.p. 173°). Galactosazone gives dehydrogalactosazone, m.p. 208°



(decomp.), which retains 1 EtOH with unusual firmness and is converted by Ac₂O in dioxan into an isomeric dehydrogalactosazone, m.p. 180°, which does not unite with EtOH, and by N₂H₄·H₂O or CH₂N₂ into a further isomeride, m.p. 212° (decomp.), which is indifferent towards EtOH. Dehydrogalactosazone diacetate has m.p. 188° (decomp.). Dehydromaltosazone, C₂₄H₃₀O₉N₄·H₂O, m.p. 246° (decomp.), yields a pentaacetate, m.p. 220° (decomp.); maltosazone pentaacetate has m.p. 159° (decomp.). Dehydrolactosazone (+1H₂O), m.p. 238° (decomp.), and its hexa-acetate, m.p. 139°, are described. H. W.

Mannans. IV. Configuration of nut- and salep-mannan and the extent of the validity of Hudson's rules of superposition among derivatives of mannose. F. KLAGES and R. MAURENBRECHER (Annalen, 1938, 535, 175—204).—Malt extract has almost equally pronounced actions towards salep- and nut- (I)-mannan, thus giving new evidence of the similar structure of these compounds, but fission of the enzyme into a di- and a poly-saccharase is not observed. With aged samples of enzyme the hydro-

lysis is frequently incomplete but cautious evaporation of the solution restores the enzymic activity almost to its original val. (I) is subjected to aceto-lysis until fission has reached 65%, the product is hydrolysed, and mannose is removed from the conc. solution as completely as possible as phenylhydrazine; the remaining solution yields *mannobiosazone* (II), $C_{24}H_{32}O_9N_6$, m.p. 136—138° (corr.) with slight previous softening, decomp. about 190° (corr.), $[\alpha]_D^{20}$ —42° in MeOH, —22° in C_5H_5N -EtOH (4 : 6). The corresponding carbohydrate could be obtained only in a syrupy although nearly homogeneous form whilst the corresponding acetate could not be caused to crystallise. The suitability of osazones for determinations of configuration is established by observations of the compounds from glucose, maltose, cellobiose, and lactose. Determinations of $[\alpha]_D$ particularly in MeOH and to a somewhat smaller extent in C_5H_5N -EtOH show satisfactory fulfilment of the rules of superposition and an unequivocal assignment of disaccharides to the α - or β -series is secured. The slight displacement (about 10°) of the observed vals. with respect to the calc. vals. is a general phenomenon with 1 : 4-disaccharides and is caused by adopting glucosazone instead of a 4-substituted derivative as standard. The positive displacement of (II) is particularly marked but the MeOH val. and the corr. C_5H_5N -EtOH val. prove conclusively the β -configuration. There is no polarimetric evidence for the presence of α -mannosidic linkings in the syrupy by-products of the prep. of (II) so that a solely β -mannosidic structure must be assigned to the various mannans. Various modes of comparison of $[\alpha]_D$ of glucosides and the corresponding polysaccharides in connexion with the application of Hudson's rules are discussed. The calculations for all glucose derivatives are considerably more accurate than those of the corresponding mannose derivatives; this is due partly to the small contribution of the $C_{(1)}$ atom of mannose derivatives towards $[\alpha]_D$ whereby the relative discrepancy for a similar abs. error is larger. A much more pronounced dependence of $[\alpha]_D$ of all investigated derivatives accompanies these discrepancies of the mannose compounds. Thus the methylated derivatives between H_2O , C_6H_6 , and $CHCl_3$ and the methylmannosides between H_2O , MeOH, and C_5H_5N -EtOH show differences of about the same order of magnitude as are caused by the replacement of non-glucosidic Me by Ac or H and the variations of $[\alpha]_D$ of methylmannan in various solvents exceed the changes by all substitutive processes. It is remarkable that by compounds so similar chemically as methylmannan and β -pentamethylmannose (or to a smaller extent as methylcellulose and β -pentamethylglucose) the transition from C_6H_6 to $CHCl_3$ causes reversed and extraordinarily pronounced displacements of rotation. It therefore appears reasonable to consider $[\alpha]_D$ as influenced by two partial causes: (a) a constitutive cause brought about by the mutual action of the atoms through the chain and corresponding approx. with $[\alpha]_D$ of the gaseous product and (b) an association or solvent cause. Since, in spite of great constitutive similarities, the solvate sheaths, e.g., around the Me groups of the glucosides and around the sugar residues of the polysaccharides,

are of widely differing natures the solvent influence on $[\alpha]_D$ of the two compounds can differ in magnitude and even in sign and thus explain the discrepancy from Hudson's rules.
H. W.

Polysaccharide produced from sucrose by *Leuconostoc dextranicum*. S. PEAT, M. STACEY, and E. SCHLÜCHTERER (Nature, 1938, 141, 876).—The purest dextran isolated is a non-reducing, H_2O -sol., white powder, $[\alpha]_D^{20} +180^\circ$ in H_2O ; hydrolysis (boiling $N-H_2SO_4$) gives a 92% yield of glucose. Methylation proceeds normally, yielding a homogeneous product, $[\alpha]_D$ 210—214° in $CHCl_3$ (OMe 44·5%), which is more stable towards hydrolysing agents than is methylated starch. Complete hydrolysis (50% aq. AcOH + 4% of conc. HCl) gave 2 : 3 : 4-trimethylglucopyranose as the principal product, establishing the nature of the link between the glucose units of dextran as being 1 : 6-glucosidic. The isolation of a small proportion of tetramethylglucoside by vac. distillation of the glucosides indicates a terminated chain.
L. S. T.

Dextrins and starch. I. K. MYRBÄCK. II. Takadiastase and maize starch. K. AHLBORG and K. MYRBÄCK. III. Trisaccharides as degradation products of starch. K. MYRBÄCK (Biochem. Z., 1938, 297, 160—171, 172—178, 179—183).—I. β -Amylase (I) converts starch into dextrins having very low reducing power, high, very greatly varying mol. wts., and very variable P contents. Approx. 40% of the starch is thus degraded. The dextrins are further degraded by α -amylase but only slowly or not at all by (I) which also does not degrade the dextrins after they have been treated with HCl.

II. The dextrins produced from maize starch by takadiastase (II) have very variable P contents and reducing powers and mol. wts. corresponding with mols. composed of 3—6 glucose residues. They are fermented as rapidly as is starch itself by dried yeast and by yeast maceration juice but not by living yeast.

III. (Cf. A., 1938, II, 128.) The dextrin fraction of mol. wt. approx. 495 obtained from maize starch by the action of (II) and similar fractions obtained from beer wort, when freed as far as possible from fermentable carbohydrates and non-carbohydrates, yield tri- and tetra-saccharides or very similar substances.
W. McC.

Analysis of diastatic split-products of starch. M. SOMOGYI (J. Biol. Chem., 1938, 124, 179—187).—Glucose is produced directly from starch or glycogen by diastase at an early stage, and is not merely a hydrolysis product of maltose produced by the action of other enzymes. The non-fermentable reducing fraction behaves as a trisaccharide, but is not homogeneous. The separate determination of glucose, maltose, and non-fermentable fraction is described.
P. G. M.

Preparation of alkoxyurethanes. J. MILIOTIS (Praktika, 1935, 10, 445—447; Chem. Zentr., 1936, ii, 1708).—Treatment of halogenated acid amides with Br and Na alkoxides yields urethanes of the corresponding alcohols. Et (cf. A., 1926, 943) and Me methoxymethylcarbamates, b.p. 89—91°/16 mm., are described.
A. H. C.

Reaction of amino-acids, peptides, and related substances with sugars. II. N. SHIGA (J. Biochem. Japan, 1938, 27, 307—334; cf. A., 1938, II, 6).—Data for the reaction between glycylalanine anhydride or ovalbumin and glucose (I) at p_H 7—9 are given and discussed. In their reactions with (I), glycine and glycylglycine behave like dipeptide and tripeptide, respectively, when H_2O is replaced by 28.6% aq. dioxan as solvent. The displacement of p_H accompanying the reactions is not indicative of the acid produced, being dependent on the buffering power of the solution. No optimum p_H for combination of NH_2 -acid with glucose appears to exist (cf. Frankel and Katchalsky, A., 1937, II, 402). F. O. H.

Formation of amino-acids from α -diketo-compounds. Glycine derivatives from glyoxal. K. MAURER and E. H. WOLTERSDORF (Z. physiol. Chem., 1938, 254, 18—24).—Glyoxal- $NaHSO_3$ with $NHEt_2$ in EtOH gives diethylaminoacetethyamide (I) [*ethiodide*, m.p. 155°; *reineckate*; *picrate*, m.p. 122° (cf. Hahn and Loos, A., 1919, i, 18)]. Similarly, from appropriate bases, were prepared diethylaminoacetamide, ethylaminoacetethyamide, and sarcosine-methylamide (II) (Abderhalden *et al.*, A., 1933, 265) [*picrate*, m.p. 175°]. Polymerised glyoxal with $NHEt_2$ in EtOH yields (I), Et diethylaminoacetate (*ethiodide*, m.p. 123—125°), and triethylbetaine; the reaction in presence of AcOH yields the ester but not the amide whilst the yield of ester+amide is increased from 40 to 65% by passing CO_2 through the reacting mixture. Polymerised glyoxal and NH_2Me in EtOH afford sarcosine Et ester and (II). F. O. H.

Compounds of mercuric chloride with betaines of biological importance. R. KRIMBERG (Biochem. Z., 1938, 297, 261—269).—Alcoholic solutions of betaine, β -homobetaine, γ -butyrobetaine, crotonobetaine, and *r*-carnitine with alcoholic solution of $HgCl_2$ yield, respectively, the following compounds: $C_3H_{11}O_2N_2, 2HgCl_2$, m.p. 183°; $C_6H_{13}O_2N_2, 3HgCl_2$, m.p. 150°; $C_7H_{15}O_2N_2, 2HgCl_2$, m.p. 185°; $C_8H_{13}O_2N_2, 2HgCl_2$, m.p. 174°; and $C_7H_{15}O_3N_2, 2HgCl_2$, m.p. 191°. Free choline does not combine with $HgCl_2$ but choline chloride gives the compound, $C_5H_{14}ONCl, 6HgCl_2$, m.p. 248°. W. McC.

Preparation of esters of carnitine and of crotonic acid betaine. E. STRACK and K. FÖRSTERLING (Ber., 1938, 71, [B], 1143—1150).—The hydrochlorides of the bases are esterified with MeOH (EtOH)-HCl and the esters are converted into their reineckates either directly or through the aurichloride or platinichloride. The reineckates are converted by Ag_2SO_4 into the corresponding sulphates from which the hydrochlorides or hydriodides are obtained by $BaCl_2$ or BaI_2 . Thus carnitine Me_2 ester gives a *hydrochloride*, m.p. 178°, *aurichloride*, m.p. 108°, *platinichloride*, m.p. 197—198° (decomp.), *reineckate*, m.p. 136°, *rhodanilate*, m.p. 154—156°, and *mercurichloride*, m.p. 110°. Carnitine Et ester yields a *hydrochloride*, m.p. 146°, *aurichloride*, m.p. 105°, *platinichloride*, m.p. 211—212° (decomp.), *reineckate*, m.p. 135—136°, *rhodanilate*, m.p. 94°, and *mercurichloride*. The *hydriodide*, m.p. 140°, *sulphate*, m.p.

121.5°, *aurichloride*, m.p. 95.5°, *platinichloride*, decomp. 186° after softening at 184°, *reineckate* (+ $1H_2O$), m.p. (anhyd.), 149°, and *rhodanilate*, m.p. 170°, of acetylcarnitine Me ester are described. Acetylcarnitine Et ester gives a *hydriodide*, m.p. 113.5°, *sulphate*, m.p. 128—129°, non-cryst. *aurichloride*, *platinichloride*, m.p. 187° after softening at 185°, *reineckate*, m.p. 150°, *rhodanilate*, m.p. 166° after softening at 163°, and *mercurichloride*, $C_{11}H_{22}O_4NCl, 6HgCl_2$, m.p. (indef.), 150—155°. Crotonobetaine Me ester affords a *hydrochloride*, m.p. 173—174°, *aurichloride*, m.p. 163°, *platinichloride*, decomp. 212—213° after softening at 210°, *reineckate*, m.p. 163°, *rhodanilate*, m.p. 171°, and *mercurichloride*, m.p. 131°. A *hydrochloride*, m.p. 150° after softening at 148°, *aurichloride*, m.p. 105°, *platinichloride*, decomp. 208°, *reineckate*, m.p. 164—166°, *rhodanilate* (+ $1COMe_2$), m.p. 132°, and *mercurichloride*, $C_9H_{18}O_2NCl, HgCl_2$, m.p. 112°, are derived from crotonobetaine Et ester. Carnitine *rhodanilate* (+ $1H_2O$), m.p. 110° after softening at 108°, *acetylcarnitine hydriodide*, m.p. 169°, and *rhodanilate* (+ $1H_2O$), m.p. 107° after softening at 204°, *crotonobetaine reineckate*, m.p. 159°, and *rhodanilate*, m.p. 135°, are described. The solubilities at 20° and 0° of the phosphotungstates of carnitine and its Me and Et ester, acetylcarnitine and its Me and Et esters, and crotonobetaine and its Me and Et esters are recorded. H. W.

Preparation of pure *d*-arginine. S. W. FOX (Science, 1938, 87, 418—419).—Essential precautions for obtaining pure *d*-arginine (I) from the hydrochloride appear to be the choice of a satisfactory protein source, *e.g.*, salmin and gelatin of good grades, but not casein, hog's blood, or defatted canned sardine spermatoc tissue, and the removal of the (I)-Ag complex from the solution of the free base. Details for a 96% recovery of pure (I) from its hydrochloride are given. (I) absorbs CO_2 from the air, but this can be removed by boiling the solution for recrystallisation. L. S. T.

Synthesis of *dl*-threonine. H. ADKINS and E. W. REEVE (J. Amer. Chem. Soc., 1938, 60, 1328—1331).— $OH \cdot N \cdot CAc \cdot CO_2Et$ (I) (modified prep.) is converted by H_2 -Raney Ni at 90—100°/120 atm. into $CO_2Et \cdot C \begin{smallmatrix} \swarrow CMe \cdot N \\ \searrow N \cdot CMe \end{smallmatrix} \cdot C \cdot CO_2Et$, but at 300 atm. gives 37% of mixed esters, $OH \cdot CHMe \cdot CH_2(NH_2) \cdot CO_2Et$, whence 50% of *dl*-threonine (II) is obtained. Et_2SO_4 and NaOH in dioxan at 75—90° convert (I) into *Et ethyloximinoacetoacetate*, b.p. 97—98°/8 mm., hydrogenation of which gives 75% of esters, giving a 50% over-all yield of (II). R. S. C.

Electrometric titration of aminoalkylsulphonic acids. P. RUMPF (Bull. Soc. chim., 1938, [v], 5, 871—887).— $NH_3^+ \cdot [CH_2]_n \cdot SO_3^-$ [$n = 0-4$, m.p. 263°; 5, m.p. 310—312°; 10, m.p. 340° (decomp.)], $NH_2 \cdot Ph \cdot [CH_2]_n \cdot SO_3^-$ ($n = 1-3$, m.p. 265°), $NMe_3^+ \cdot [CH_2]_2 \cdot SO_3^-$ (cf. Cortese, A., 1936, 459), $(NH_3^+) \cdot CHMe \cdot CH_2 \cdot SO_3^-$, $C \cdot Ph \cdot [C_6H_4 \cdot NH \cdot (CH_2)_2 \cdot SO_3^-]_2 \cdot H^+$, are prepared, by improved methods in many cases. Electrometric titration shows that basicities increase

with the no. of CH_2 separating the two ionic groups, rapidly at first and then approaching a limit.

A. T. P.

Bridged derivatives of trimethylarsine with palladous halides.—See A., 1938, I, 388.

Hydrides of boron. IX. Preparation of some methyltriborinetriamines. H. I. SCHLESINGER, D. M. RITTER, and A. B. BURG (J. Amer. Chem. Soc., 1938, 60, 1296—1300; cf. A., 1938, I, 207).—The cyclic structure of $(\text{BH}\cdot\text{NH})_3$ (I) is confirmed by prep. of the theoretical no. of Me derivatives. (I) is best (41.5% yield) prepared from B_2H_6 and NH_3 at $200^\circ/100$ atm. during 15 min. With NH_3 and NH_2Me B_2H_6 gives mixtures of (I), its N-Me (II), b.p. 84° , NN'-Me₂, b.p. 108° , and NN'N''-Me₃ derivative (III), b.p. 134° . In absence of NH_3 only (III) and the liquid compound, $\text{B}_2\text{H}_6\cdot 2\text{NH}_2\text{Me}$, are obtained. $\text{BMe}_2\cdot\text{NH}_2$ with (I) gives rather small amounts of B-Me, BB'-Me₂, and BB'B''-Me₃ derivatives, H_2 , solid by-products, and, occasionally, CH_4 . BMe_3 and (I) or (II) give the NB-Me₂, b.p. 124° , NBB'-Me₃, b.p. 139° , and NBB'B''-Me₄ derivative, b.p. 158° . The compounds, particularly (I), are associated in the vapour phase. Homogeneity of the products is proved by agreement of the determined v.p. with those deduced from the Clapeyron-Clausius equation.

R. S. C.

Reducing action of Grignard reagents on acyl chlorides. F. C. WHITMORE (Rec. trav. chim., 1938, 57, 562—568).—Adding RCOCl (1 mol.) to $\text{MgBu}^\gamma\text{Cl}$ (4 mols.) gives $\text{CH}_2\text{R}\cdot\text{OH}$, $\text{CHBu}^\gamma\text{R}\cdot\text{OH}$, and *iso*- C_4H_8 (2 mols. for each $\text{CH}_2\text{R}\cdot\text{OH}$ and 1 mol. for each $\text{CHBu}^\gamma\text{R}\cdot\text{OH}$); the reaction involves (a) reduction of RCOCl successively to RCHO and $\text{CH}_2\text{R}\cdot\text{OH}$, with addition of $\text{MgBu}^\gamma\text{Cl}$ to RCHO , or (b) reduction of RCOCl to $\text{CH}_2\text{R}\cdot\text{OH}$, formation of the ketone from RCOCl , and reduction of the ketone. Thus, $\text{Pr}^\alpha\text{COCl}$, $\text{Pr}^\beta\text{COCl}$, and $\text{Bu}^\gamma\text{COCl}$ give 9, 20, and 94% of $\text{CH}_2\text{R}\cdot\text{OH}$ and 71, 63, and 1.5%, respectively, of $\text{CHBu}^\gamma\text{R}\cdot\text{OH}$. Adding $\text{Bu}^\gamma\text{COCl}$ (0.22 mol.) to $\text{MgBu}^\gamma\text{Cl}$ (0.1 mol.) gives *iso*- C_4H_8 (0.27 mol.) and 45% each of $\text{CH}_2\text{Bu}^\gamma\text{OH}$ and $\text{Bu}^\gamma\text{CO}_2\cdot\text{CH}_2\text{Bu}^\gamma$. Adding $\text{MgBu}^\gamma\text{Cl}$ (1.5 mols.) to $\text{Bu}^\gamma\text{COCl}$ (8 mols.) and keeping at -10° gives only $\text{Bu}^\gamma\text{CO}_2\cdot\text{CH}_2\text{Bu}^\gamma$ (8%), *iso*- C_4H_8 (17%), and COBu^γ_2 (32%), 6.2 mols. of $\text{Bu}^\gamma\text{CO}_2\text{H}$ being recovered. Adding $\text{MgBu}^\gamma\text{Cl}$ (2.5 mols.) to AcCl (3.2 mols.) gives *iso*- C_4H_8 (8%), EtOAc (9.5%), pinacolone (17%), and pinacolyl acetate (6.6%). Heating AcCl and anhyd. MgCl_2 in dry Et_2O for 4 days gives only 10% of EtOAc and (?) EtCl . Reduction is not confined to $\text{MgBu}^\gamma\text{Cl}$; thus, adding AcCl (2 mols.) to $\text{MgBu}^\alpha\text{Br}$ (5 mols.) gives C_4H_8 , EtOH (8%), and β -hexanol (13%). Adding $\text{Bu}^\gamma\text{COCl}$ (1 mol.) to $\text{MgBu}^\alpha\text{Br}$ (4 mols.) gives $\text{CH}_2\text{Bu}^\gamma\text{OH}$ (27%), $\text{CHBu}^\alpha\text{Bu}^\gamma\text{OH}$ (69%), and C_4H_8 , but no $\text{CH}_2\text{Bu}^\alpha\text{OH}$. Adding MeCHO (2 mols.) to $\text{MgBu}^\alpha\text{Br}$ (5 mols.) gives EtOH (20—25%), β -hexanol (34%), and some C_4H_8 ; $\text{MgBu}^\gamma\text{Cl}$ similarly gives EtOH (22%) and pinacolyl acetate (56%), so that branching in the Bu is seen to have little effect. Adding $\text{Bu}^\gamma\text{CO}_2\text{Et}$ (1 mol.) to $\text{MgBu}^\alpha\text{Br}$ (4 mols.) gives C_4H_8 and $\text{CHBu}^\alpha\text{Bu}^\gamma\text{OH}$ (40—45%), but no $\text{CH}_2\text{Bu}^\gamma\text{OH}$.

R. S. C.

Organocalcium iodides. C. GLACET (Bull. Soc. Chim., 1938, [v], 5, 895—900).— EtI and Ca in Et_2O yield a 1:1 mixture of $(\text{Et}_2\text{O})_2\text{CaI}_2$ and Et_3OCaI . MeI , Pr^αI , BuI , $\text{CH}_2\text{CH}\cdot\text{CH}_2\text{I}$, $\text{CH}_2\text{Bu}^\beta\text{I}$, $n\text{-C}_8\text{H}_{17}\text{I}$, PhI , and *m*- $\text{C}_6\text{H}_4\text{MeI}$ react easily with Ca . Pr^βI and *sec*- BuI react with difficulty and Bu^γI and CMe_2EtI not at all. The organo-Ca derivatives react normally with aldehydes, ketones, nitriles, and acid esters, but not with acid chlorides; e.g., PhCHO and the respective Ca derivative yields $\text{CHPhR}\cdot\text{OH}$ ($\text{R}=\text{Me}$, Et ; Pr ; $\text{CH}_2\text{Bu}^\beta$; Ph); COMeEt and BuI-Ca give $\text{CMeEtBu}^\alpha\text{OH}$ and $\text{COPh}_2\text{-PhI-Ca}$ yield CPh_3OH ; MeCN and PhCN , and EtI-Ca , afford COMeEt and COEtPh , respectively; HCO_2Et (EtOAc) and EtI-Ca afford CHEt_2OH (CMeEt_2OH), and EtOBz-PhI-Ca give CPh_3OH and some CHPh_3 (cf. A., 1926, 1130).

A. T. P.

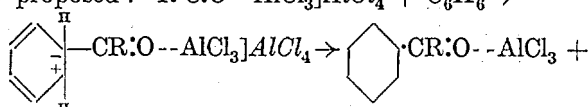
Reactivity of substituents in benzene derivatives. I, II. A. MANGINI (Ric. sci. Progr. teen., 1935, 6, II, 344, 439—440; Chem. Zentr., 1936, ii, 601—602).—Reactivity is correlated with dipole moment with special reference to compounds containing ≤ 3 substituents.

H. N. R.

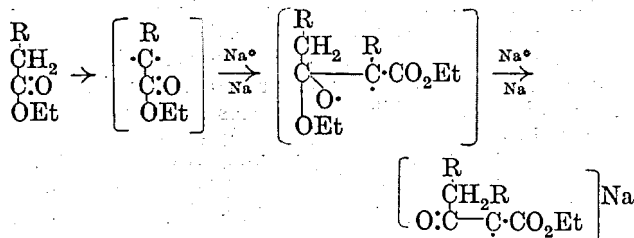
Advances in the Friedel-Crafts reaction and its technical application. P. KRANZLEIN (Angew. Chem., 1938, 51, 373—381).—A lecture dealing with the use of AlCl_3 in the synthesis of hydrocarbons and its applications in the oil and artificial resin industries, in the synthesis of aldehydes and, most extensively, of ketones.

H. W.

Positive hydrogen atoms. IX. Friedel-Crafts and ethyl acetoacetate syntheses. A parallel and a proposed reaction mechanism. W. DILTHEY (Ber., 1938, 71, [B], 1350—1353).—For the Friedel-Crafts reaction the following mechanism is proposed: $\text{R}\cdot\text{C}\cdot\text{O}-\text{AlCl}_3\text{AlCl}_4 + \text{C}_6\text{H}_6 \rightarrow$



$\text{HCl} + \text{AlCl}_3$. It is thus obvious that AlCl_3 attached to O of COCl remains attached in the final product and hence cannot act as a catalyst whereas the italicised mol. AlCl_3 behaves as a catalyst since it is continuously re-formed from the very unstable $\text{AlCl}_3\text{-HCl}$. It is thus obvious why >1 mol. of AlCl_3 must be used and why often only a very slight excess suffices. The acetoacetic synthesis is formulated:



+ Na^*OEt . The ionoid adduct immediately decomposes with elimination of NaOEt , which can then form a new salt with EtOAc . The Na^* functions as catalyst.

H. W.

Halogenation of aromatic and aliphatic compounds. R. ODA, K. TAMURA, and K. IMAI (Sci.

Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 596—618).—2-Me increases, but 9-Br, 9-NO₂, 2-Cl, and 2-CO₂H decrease, the rate of addition of Br to anthracene in AcOH. 7-Cl decreases slightly the very rapid reaction of Na anthracene-2-sulphonate with Br in H₂O. 2-Hydroxy- and -amino-anthracene absorb Br rapidly, but not instantaneously. *o*- and *p*-OH·C₆H₄·CHO react with Br in AcOH at the same rate, but more slowly than does *m*-OH·C₆H₄·CHO; this and the ability of the *m*-compound to undergo the Cannizzaro reaction may be connected with ability of the *o*- and *p*-compounds to exist in the keto-form. The following relative rates of reaction with Br in AcOH are established: saligenin > CH₂·CH·CH₂·OH > CHPh·CH·CH₂·OH; CH₂Ph·OH does not react in AcOH. Dipentene, linoleic acid, geraniol, and linalool react with 1 mol. of Br₂ in AcOH instantaneously, but relatively slowly with the second mol. The relation between rate of absorption of Br and structure is discussed, with particular reference to the purity of oleic acid and the ease of coupling.

β-C₁₀H₇·OH reacts rapidly with (SCN)₂; oleic acid, cyclohexene, and anthracene react more slowly; PhOH and NH₂Ph barely react. (SCN)₂ is a less potent cationoid reagent than is Br. Results obtained by Brunner's method, but using 2 mols. of KI, are very similar to those obtained using 1 mol. 9-Nitroanthracene reacts more rapidly with NaO·C₅H₁₁ than with NaOEt, and still more slowly with NaOMe.

R. S. C.

Condensations by sodium. XIII. Wurtz-Fittig synthesis of amylbenzene and reactions of sodium benzyl. A. A. MORTON and F. FALLWELL, jun. (J. Amer. Chem. Soc., 1938, 60, 1429—1431).—C₅H₁₁Na and PhCl give little C₅H₁₁Ph, even if the C₅H₁₁Cl and PhCl are added together to Na; the main product is a *polymeride*, b.p. 155—165°/4 mm., containing 1 C₅H₁₁ and 3 Ph, and probably formed by disproportionation to C₆H₁₂ and C₆H₄<. Further, NaPh reacts very incompletely with C₅H₁₁Cl or PhCl. When NaPh is prepared from C₅H₁₁Cl and Na in C₆H₆, converted by PhMe into CH₂PhNa, and caused to react with BuCl or C₅H₁₁Cl at 75°, 70% of C₅H₁₁Ph or 61% of C₆H₁₃Ph, respectively, is formed. CH₂Cl₂ similarly gives 18% of CH₂(CH₂Ph)₂, and MeI or EtBr gives PhEt or PhPr, respectively. The greater reactivity of CH₂PhNa is, however, not general, for NaPh reacts quantitatively with I, PhMe, or CO₂; with (CH₂O)₃, C₅H₁₁Na, NaPh, and CH₂PhNa give 28% of C₆H₁₃·OH, 19% of CH₂Ph·OH, and 17% of CH₂Ph·CH₂·OH, respectively.

R. S. C.

Condensation of aliphatic alcohols with aromatic hydrocarbons. I. Preparation of mesitylene and *s*-triethylbenzene. J. F. NORRIS and J. N. INGRAHAM (J. Amer. Chem. Soc., 1938, 60, 1421—1423).—Alcohols and AlCl₃ react to give AlCl₂·OR, which decomposes, when heated, into RCl and AlOCl. The mixture is thus effective for alkylation of aromatic hydrocarbons. When alkyl halides are used, <1 mol. of AlCl₃ per mol. of C₆H₆ gives a complex mixture, but 2 mols. of AlCl₃, 3 of RCl, and 1 of C₆H₆ give mainly *s*-C₆H₃R₃. Similarly, addition of MeOH (1.33 mols.) and PhMe (0.33 mol.) to PhMe (0.33 mol.) and AlCl₃ (2.66 mols.) at 10—15° and subsequent

heating at 110° give a good yield of *s*-C₆H₃Me₃, obtained in better yield from *m*-xylene, MeOH, and AlCl₃ in the mol. proportions 1:1:3. EtOH and C₆H₆ similarly give *s*-C₆H₃Et₃, b.p. 214.8°/755.1 mm. (corr.), the identity of which is proved by prep. of the Br₂-, m.p. 104.6—104.8°, and (NO₂)₃-derivative, m.p. 112.4—112.6°, and by oxidation to *s*-C₆H₃(CO₂H)₃.

R. S. C.

Influence of directing groups on nuclear reactivity in oriented aromatic substitution. IV. Nitration of the halogenobenzenes. M. L. BIRD and C. K. INGOLD (J.C.S., 1938, 918—929; cf. A., 1931, 1405).—Rates of nitration are determined in terms of the rate of nitration in C₆H₆; e.g., in AcNO₃-Ac₂O at 18° (C₆H₆ = 1): PhF, 0.15; PhCl, 0.033; PhBr, 0.030; PhI, ~0.18. The difference in the rates of nuclear and side-chain substitution is attributed to the greater relative importance of polarisability effects, particularly the electromeric, in the former case; it is deduced that these effects collectively are electron-releasing in the order I > Br > Cl > F. Nitrations of PhCl and PhBr (+ C₆H₆) by AcNO₃ in excess of Ac₂O, MeCN, or MeNO₂ at 0°, 25°, and 35° are examined in detail. Solvent effect on the relative reaction rates is small and irregular, but the temp. effect is large and regular. It shows that the orienting substituents alter reaction rates at the several nuclear positions mainly by changing the energies of activation.

A. T. P.

Action of alcoholic alkali on polychloro- and polybromo-benzenes in methyl ethyl ketone. T. VAN DER LINDEN (Rec. trav. chim., 1938, 57, 781—788).—NaOMe in COMeEt converts C₆Br₆ into C₆HBr₅ and C₆HBr₅ into C₆H₂Br₄ (80% of which is the 1:2:4:5-compound), but has little effect on less brominated benzenes. Reaction in COMe₂ is similar, but in EtOH and, more so, in C₅H₁₁·OH or C₆H₆ is slower. In COMeEt C₆Cl₆ and NaOMe give C₆Cl₅·OMe, less chlorinated benzenes being substantially unaffected.

R. S. C.

Reduction reactions of *p*-dinitrobenzene. I. ANTENER (Helv. Chim. Acta, 1938, 21, 812—816).—*p*-C₆H₄(NO₂)₂ is converted by boiling NaOMe-MeOH into 4:4'-dimethoxyazobenzene, m.p. 116°, and *p*-nitroanisole, m.p. 53°. In alkaline solution *p*-C₆H₄(NO₂)₂ is reduced by glucose to 4:4'-dinitroazoxybenzene, m.p. 200°, and 4:4'-dinitroazobenzene, m.p. 220°.

H. W.

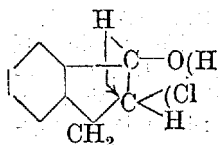
Nitration of benzenesulphonyl chloride and fluoride. G. M. BENNETT and P. V. YOULE (J.C.S., 1938, 887—893).—PhSO₂Cl and abs. HNO₃-H₂SO₄ at 30° afford a nitration product, converted (96%) by NH₂Ph into mixed nitrobenzenesulphanilides (80% *m*-NO₂-derivative from C₆H₅), analysed by thermal means, using the thaw-point device (A., 1936, 1241), or by extraction with amyl valerate at 20° and examination of vals. of *n*. Anomalous results by the latter method are due to the presence of 2:4:6-trinitro-3-hydroxydiphenylamine (I) [*2-chloro-3:4:6-trinitro-diphenylamine* has m.p. 147—148° (3-*piperidino*-derivative, m.p. 161—162°)]. The analyses show *m*- (Na salt, anhyd. and +2H₂O), 91.3±0.5; *o*- (Na salt, anhyd. and +2H₂O), 5.2±1; and *p*-, 1.8±1%, -NO₂·C₆H₄·SO₂·NHPh (cryst. forms examined), with

1.7±1% of (I). PhSO_2F gives 95.6% of *m*- NO_2 -derivative (thermal method); *p*-, m.p. 79°, and *o*-, m.p. 59°, $-\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{F}$, are described. Fuming HNO_3 and *pp'*-($\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}$)₂, new m.p. 181° (sulphoxide, m.p. 177—179°; sulphone, m.p. 251—254°), give the sulphonic acid, converted through the chloride into *p*-nitrobenzenesulphonanilide, m.p. 171° (anhyd. Na salt). A. T. P.

Preparation of disaccharine. (Derivatives of *mm'*-ditolyl.) M. DOMINIKIEWICZ and M. KIJEW-SKA (Arch. Chem. Farm., 1936, 3, 27—33; Chem. Zentr., 1936, ii, 1719).—Tetrazotised *mm'*-dimethylbenzidine is converted by SO_2 in presence of Cu powder into 3:3'-ditolyl-4:4'-disulphinic acid, decomp. 150°, and thence by oxidation ($\text{KMnO}_4\text{--K}_2\text{CO}_3$) into 3:3'-ditolyl-4:4'-disulphonic acid (*K* salt, m.p. >300°), which with PCl_5 affords the disulphonyl chloride, m.p. 164—166°, and this with $(\text{NH}_4)_2\text{CO}_3$ at 150° the diamide (I), resinifies at 230—240°. Oxidation of (I) to the dibasic acid was not achieved.

A. H. C.

Reactions of indene dichloride and the *cis*- and *trans*-chlorohydrins. Mechanism of ketone formation. C. M. SUTER and G. A. LUTZ (J. Amer. Chem. Soc., 1938, 60, 1360—1365).—Indene and Cl_2 in CCl_4 give a homogeneous dichloride (I), b.p. 83—85°/2 mm., obtained also by PCl_5 from the *trans*-chlorohydrin (II) and by SOCl_2 from (II) or its *cis*-isomeride (III). Hydrolysis of (I) gives mostly (II) with some (III). Pyrolysis of (I) at 225—235° gives HCl and 37% of 2-chloroindene (IV), a trace being formed also by distillation in vac. HgCl_2 in MeNO_2 probably does not affect (I). Pt-hydrogenation of (IV) gives indane; conc. H_2SO_4 resinifies it slowly. P_2O_5 in CCl_4 converts (II) and (III) into (IV), but under certain conditions (II) gives an ether, $\text{C}_{18}\text{H}_{16}\text{OCl}_2$, b.p. 153—155°/3 mm., which with Br gives HBr and a compound, decomposed at the b.p./760 mm. into (IV). (III) yields indan-1-one in H_2O at <80°, the rate of reaction being unaffected by alkali, but greatly accelerated by alkali or Ag^+ (removes HCl); the reaction mechanism is thus that illustrated in the annexed formula. Ag^+ is without effect on (II), which in slightly alkaline solution at 100° gives mostly indan-2-one, reaction occurring by way of the ether. (II) and, more readily, (III) give indan-1-one in dil. H_2SO_4 . With aq. NaOAc (III) gives a mixture, containing mostly the *trans*-glycol, but no ketone. R. S. C.



Constitution of monobromodialene [bromodihydronaphthalene]. H. A. WEIDLICH (Ber., 1938, 71, [B], 1201—1202).—The product obtained by loss of HBr from 1:2-dibromo-1:2:3:4-tetrahydronaphthalene is 2-bromo-3:4-dihydronaphthalene (I) since it is converted by Mg in Et_2O followed by CO_2 into 3:4-dihydro-2-naphthoic acid, $\beta\text{-C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$, C_{10}H_8 , and 2:2'-di-3:4:3':4'-dihydrodinaphthyl (II). Further the Mg derivative of (I) and 1-keto-1:2:3:4-tetrahydronaphthalene yield (II) and 2:1'-di-3:4:3':4'-dihydrodinaphthyl, m.p. 87°, dehydrogenated (Pd-C at 300°) to 2:1'-dinaphthyl. H. W.

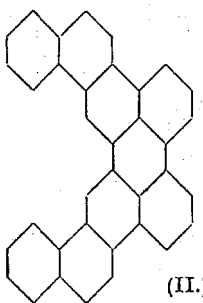
Halogenation. XX. Halogenation of fluorene. P. S. VARMA and V. S. RAO (J. Indian Chem. Soc., 1938, 15, 72—76; cf. A., 1937, II, 331).—2-Chloro-7-bromofluorene, m.p. 157°, is obtained by brominating 2-chlorofluorene (I) (prep. by Cl_2 and a little I in C_6H_6 at 80—90°) in presence of a little Fe in CHCl_3 , by chlorinating 2-bromofluorene (II) with a little I in CHCl_3 in light, and by diazo-reactions from 2-chloro-(III) or 2-bromo-7-aminofluorene (IV). Addition of HNO_3 -oleum to (I) and I in AcOH and heating at 100° gives 2-chloro-7-iodofluorene, m.p. 122°, also obtained from (III) and by a diazo-reaction, applied to the reduction product (not isolated) of 2-iodo-7-nitrofluorene. 2-Bromo-7-iodofluorene, m.p. 162°, is prepared by HNO_3 -oleum from I and (II) or (IV) and by a diazo-reaction from 2-iodo-7-aminofluorene (V). Iodination, as above, of 2:7-dibromofluorene gives 2:7-dibromo-x-iodofluorene, m.p. 146.5°. The Cl_2 -compound gives 2:7-dichloro-x-bromofluorene, m.p. 143°. 2:7-Di-iodofluorene, m.p. 155.5°, is prepared from 2:7-diaminofluorene, from (V), and by iodination, as above, of fluorene in boiling AcOH .

R. S. C.

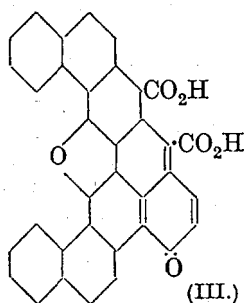
Synthesis of condensed ring systems. I. H. A. WEIDLICH (Ber., 1938, 71, [B], 1203—1209).—Dodecahydraphenanthrene-9:10-dicarboxylic anhydride, readily obtained from octahydrodiphenyl and maleic anhydride (I), is converted by Br in CHCl_3 into octahydrophenanthrene-9:10-dicarboxylic anhydride, m.p. 310°, dehydrogenated (Pd-C at 300°) to phenanthrene-9:10-dicarboxylic anhydride, m.p. 321°. 1:1'-Di-3:4:3':4'-dihydrodinaphthyl and (I) in boiling PhNO_2 give octahydro-3:4:5:6-dibenzphenanthrene-9:10-dicarboxylic anhydride, m.p. 254° [corresponding acid, m.p. 125° (decomp.), and its Me_2 ester, m.p. 172°], which with Br in CHCl_3 gives tetrahydro-3:4:5:6-dibenzphenanthrene-9:10-dicarboxylic anhydride (II), m.p. 282° (corresponding, very unstable acid and its Me_2 ester, m.p. 243°); this is decarboxylated by Cu powder in boiling quinoline to tetrahydro-3:4:5:6-dibenzphenanthrene, b.p. 180°/0.1 mm., m.p. 142°. Dehydrogenation (Pd-C at 300°) of (II) affords 3:4:5:6-dibenzphenanthrene-9:10-dicarboxylic anhydride, m.p. >360°. 3:4:5:6-Dibenzphenanthrene, m.p. 177°, is best obtained by heating (II) with Cu powder, anhyd. Ba(OH)_2 , and SnCl_2 at ~400° in N_2 , distillation, and treatment of the distillate with S at 250—300°; in the absence of SnCl_2 and presence of air, the main product is 1:12-benzperylene, m.p. 372°. 2:2'-Di-3:4:3':4'-dihydrodinaphthyl and (I) in boiling xylene give octahydro-picene-9:10-dicarboxylic anhydride, m.p. 217—218°, whence (Br in $\text{CHCl}_3\text{--AcOH}$) tetrahydropicene-9:10-dicarboxylic anhydride, m.p. 309°, converted by Cu powder and anhyd. Ba(OH)_2 at 400° followed by Pd-C at 300° into picene. 1:2'-Di-3:4:3':4'-dihydrodinaphthyl and (I) in boiling xylene yield octahydro-1:2:5:6-dibenzphenanthrenedicarboxylic anhydride, flat prisms, m.p. 208°, or yellow needles, m.p. 236°, whence tetrahydro-1:2:5:6-dibenzphenanthrenedicarboxylic anhydride, m.p. 228—229°, and 1:2:5:6-dibenzphenanthrene, m.p. 122°. H. W.

Dinaphthoperylene. Chemistry of chrysene. B. SCHIEDT (Ber., 1938, 71, [B], 1248—1253).—

Gradual addition of AlCl_3 to ehrysene (I) suspended in C_6H_6 at 60° gives dinaphthoperylene (II), m.p. 240° , which is oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH to 2 : 3-10 : 11-dinaphtho-1 : 12-furanoperylene-3 : 9-quinone (or its H_2 -derivative), m.p. 288° ; this does not react with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and hence is not an *o*-quinone and is reduced by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. The furan O is identified by reductive acetylation, whereby a triacetate, $\text{C}_{42}\text{H}_{25}\text{O}_6$, m.p. 287° , is produced. In addition



(II.)



(III.)

to the quinone a ketodicarboxylic acid (III), m.p. 268° (decomp.), is produced which is readily reduced (Zn dust in AcOH - $\text{C}_5\text{H}_5\text{N}$ or $\text{NHPH} \cdot \text{NH}_2$ in AcOH - $\text{C}_5\text{H}_5\text{N}$) to a substance, $\text{C}_{35}\text{H}_{18}\text{O}_6$, m.p. 330° (*Ac* derivative, m.p. 291°). (III) is transformed by molten alkali into phenanthrene-1-carboxylic acid, m.p. 232° , and a phenanthrenedicarboxylic acid, m.p. 318° , from which an anhydride could not be derived. Finely divided (I) is converted by BzCl and AlCl_3 in CS_2 into tribenzoyldinaphthoperylene, m.p. 227° , by SO_2Cl_2 in C_6H_6 into trichlorodinaphthoperylene, m.p. 266° , and by conc. HNO_3 in AcOH at 100° into trinitrodinaphthoperylene, m.p. 262° . (I) and SO_2Cl_2 in PhNO_2 at room temp. and then at 100° afford dichlorochrysene, m.p. 270° , oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH to 8-chlorochrysene-1 : 2-quinone, m.p. 248° , which with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in boiling AcOH gives the azine, $\text{C}_{24}\text{H}_{12}\text{N}_2\text{Cl}$, m.p. 243° . H. W.

Hydrophenanthrenes. J. R. DURLAND and H. ADKINS (J. Amer. Chem. Soc., 1938, 60, 1501—1505).—Hydrogenation of phenanthrene in EtOH in presence of Raney Ni gives 91% of the 9 : 10- H_2 - (I), b.p. $162^\circ/10$ mm., and 4% of the 1 : 2 : 3 : 4- H_4 -derivative (II), b.p. 170 — $171^\circ/10$ mm., m.p. 34 — 35° (picrate, m.p. 110 — 111°). If, however, a mixture of 2 mols. of H_2 and sufficient N_2 to give 100 atm. is used, hydrogenation at 110° gives 33—40% of (II), 43% of (I), and a little H_8 -compound. The 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8- H_8 -derivative (III), b.p. $161^\circ/10$ mm., is obtained at 100° , but the 1 : 2 : 3 : 4 : 9 : 10 : 13 : 14- H_8 -compound (IV), b.p. $145^\circ/10$ mm., is formed at 130° in methylcyclohexane in 25—29% yield with twice its wt. of (III). 60—70% of the $\Delta^{11:12}\text{-H}_{12}$ -derivative (V), b.p. $134^\circ/10$ mm., is obtained at 200° with 26% of H_8 -compounds and 5—10% of H_{14} -compound (VI), b.p. $131^\circ/10$ mm. Hydrogenation of (I) to (III) involves migration of H. Accordingly, (I) is disproportionated by Raney Ni in N_2 , giving good yields of (II); the reaction proceeds with increasing velocity as the temp. is raised from 150° to 250° . (III) and (IV) are similarly isomerised at 130° , (III) being the more stable. H-migration occurs in two ways in the case of (V): a slow dispropor-

portionation to (VI) and H_8 -compounds, and a shift in the position of the ethylenic linking take place during distillation. $\text{Cu-Cr}_2\text{O}_3$ causes most of the above-mentioned reactions, but, except for the prep. of (I), gives poorer yields and requires a 50— 100° higher temp. In particular, in the H_2 - N_2 prep. of (II) the temp. necessary depends on the pressure with $\text{Cu-Cr}_2\text{O}_3$, but not with Raney Ni, and with the former catalyst reaction is never complete. The structure of (V) is uncertain, depending on absorption of 1 mol. of H_2 (Raney Ni; 240°) to give (VI), analysis, and correspondence of *n* and *d* with recorded data; presence of 5—10% of (III), (IV), or (VI) is not excluded and rigid purification is impossible owing to migration of H. O_3 in CCl_4 at 0° gives (?) $\alpha\beta$ -di-2-ketocyclohexylethane [bis-2 : 4-dinitrophenylhydrazones (VII), m.p. 242 — 243° (decomp.); a dinitrophenylhydrazones, m.p. 112 — 114° , and a small amount of acid were also formed]. With Raney Ni- H_2 at $150^\circ/100$ — 125 atm. (VII) absorbs 16 H_2 , giving $\text{C}_6\text{H}_3(\text{NH}_2)_3$ and 2 : 3 : 5 : 6-ditetramethylenehexahydroazepine, b.p. 107 — $110^\circ/2$ mm. (hydrochloride, m.p. 256 — 257° ; α -naphthyl-, m.p. 153 — 154° , and phenylcarbamide, m.p. 165 — 167°), also obtained by H_2 -Raney Ni in dioxan at $220^\circ/200$ — 250 atm. from *oo*-diaminodibenzyl, m.p. 73 — 75° [picrate, m.p. 226 — 230° ; benzoate, m.p. 255 — 257° ; prep. from the *oo*-(NO_2) $_2$ -compound by H_2 -Raney Ni at $100^\circ/100$ atm.]. This necessitates presence of the $\Delta^{12:13}\text{-H}_{12}$ -compound in (V); the yield of (VII) is, however, only 12%, but is increased by previously heating (V) for a long time, thus proving the isomerisation of (V) and the origin of (VII) in the product formed. Separation of the H-derivatives by distillation is sometimes difficult (b.p. are given for 6, 10, 13, and 26 mm., with details of technique); phenanthrene and (II) are best separated by crystallisation, (I) and (II) by way of the picrate, and (III) and (IV) by distilling at 10—13 mm. (II) and (V) cannot be completely separated. Any desired H-derivative can be prepared in quantity by choice of method. R. S. C.

$\Delta^{2:4}$ -Cholestadiene: its photochemical transformation. A. BUTENANDT and H. KUDSSUS (Z. physiol. Chem., 1938, 253, 224; cf. A., 1938, II, 270).—The formula given for cholesterylene is to be replaced by that of a $\Delta^{3:5}$ -cholestadiene.

W. McC.

Preparation of β -*p*-hydroxyphenylisopropylmethylamine.—See B., 1938, 764.

Derivatives of cyclohexylamine.—See B., 1938, 764.

Walden rearrangement. II. Reaction of *cis*- and *trans*-2-aminodicyclopentyl with nitrous acid. W. HÜCKEL, A. GROSS, and W. DOLL (Rec. trav. chim., 1938, 57, 555—561; cf. A., 1938, II, 50).—In this series, the reaction with HNO_2 is anomalous. Na-EtOH reduces the oxime, m.p. 82° (Bz derivative, m.p. 70°), of 2-ketodicyclopentyl, b.p. $232^\circ/740$ mm., $97^\circ/10$ mm., m.p. -30° (semicarbazone, m.p. 208 — 210°), to *trans*-2-aminodicyclopentyl (I), b.p. 96 — $97^\circ/10$ mm. (Bz, forms, m.p. 148° and 152° , and *Ac* derivative, m.p. 116°), whereas H_2 -Pt-black or, better, H_2 - PtO_2 in AcOH gives about 20% of (I) and 80% of the *cis*-isomeride, b.p. 108 —

111°/20 mm. (Bz, m.p. 128°, and Ac derivative). HNO₂ causes complete inversion, the *trans*- and *cis*-bases giving only the *cis*- and *trans*-alcohols, respectively, with about 50% of 1-cyclopentyl-Δ¹-cyclopentene. The following revised data are given: *cis*-, m.p. 55° (H phthalate, m.p. 126°; phenylurethane, m.p. 110°; *p*-nitro-, m.p. 83°, *p*-benzamido-, m.p. 141—142°, and *p*-amino-benzoate, m.p. 50°), and *trans*-2-hydroxydicyclopentyl, m.p. 8.5° (phenylurethane, m.p. 93—94°; *p*-nitro-, m.p. 78—79°, *p*-amino-, m.p. 72°, and *p*-benzamido-benzoate, m.p. 145—146°), best characterised by, and separated by way of, the 3:5-dinitrobenzoates, m.p. 144—145° and 76—78°, respectively. R. S. C.

Identification of alkylbenzenes. II. Identification of the eight amylbenzenes and cyclopentylbenzene by means of their mono- and diacetamido- and monobenzamido-derivatives. V. N. IPATIEV and L. SCHMERLING (J. Amer. Chem. Soc., 1938, 60, 1476—1479).—The amylbenzenes and cyclopentylbenzene (0.5—1 c.c.) are readily identified by their *p*-NHAc-, *p*-NHBz-, and (NHAc)₂-derivatives (method: A., 1937, II, 331). Mixed m.p. depressions are satisfactory. Some *o*-nitration also occurs if the substituent is CHRR' (R and R' are not H), but the *o*-NHAc-derivatives are readily removed, being much more sol. The separation of *o*- and *p*-NHBz-derivatives is sometimes difficult. The (NHBz)₂-derivatives have undesirably high m.p. The following are described: *p*-, m.p. 101—102°, and *o*-acetamido-, m.p. 79—80°, *p*-, m.p. 128—129°, and *o*-benzamido-, m.p. 99° (relationship established by interconversion), and 2:4-diacetamido-*n*-amylbenzene, m.p. 202°; *p*-acetamido-, m.p. 114°, *p*-benzamido-, m.p. 151° [obtained from *p*-iso-C₅H₁₁·C₆H₄·NH₂ (I); from *iso*-C₅H₁₁Ph only a mixture, m.p. 132—136°, of *o*- and *p*-derivatives was obtained], and 2:4-diacetamido-isoamylbenzene, m.p. 215—216°; *p*-acetamido-, m.p. 115—116°, *p*-benzamido-, new m.p. 126°, and 2:4-diacetamido-β-methyl-*n*-butylbenzene, m.p. 193—194°; *p*-acetamido-, m.p. 107°, *p*-benzamido-, m.p. 127—128°, and 2:4-diacetamido-sec.-amylbenzene, m.p. 181—182°; *p*-acetamido-, m.p. 147—148°, *p*-benzamido-, m.p. 141—142°, and 2:4-diacetamido-sec.-isoamylbenzene, m.p. (anhyd.) 193° and (+xH₂O) 189°; *p*-acetamido-, m.p. 145—146°, *p*-benzamido-, m.p. 154°, and 2:4-diacetamido-α-ethyl-*n*-propylbenzene, m.p. 199—200°; *p*-acetamido-, m.p. 164°, *p*-benzamido-, m.p. 164—165°, and 2:4-diacetamido-ββ-dimethyl-*n*-propylbenzene, m.p. 240—241°; *p*-acetamido-, m.p. 141—142°, *p*-benzamido-, m.p. 112—113° (lit. 158°), and 2:4-diacetamido-tert.-amylbenzene, anhyd., m.p. 180—181°, and +0.5H₂O, forms, m.p. 169—170° and 179—180°; *p*-acetamido-, m.p. 134°, *p*-benzamido-, m.p. 154°, and 2:4-diacetamido-cyclopentylbenzene, m.p. 228°. H₂SO₄-HNO₃ converts (I) at 0° into 3-nitro-4-isoamylaniline, m.p. 90°. R. S. C.

Karrer's theory of coupling. W. J. HICKINBOTTOM and E. W. LAMBERT (Nature, 1938, 141, 1056).—Di-*n*- (I) and diiso-butylaniline (II) and diisoamylaniline (III) couple normally with diazo-sulphanilic acid without loss of alkyl. Karrer's observations (A., 1915, i, 1073) are thus untrustworthy,

and there is no experimental basis for his theory of coupling. Contrary to Karrer (*loc. cit.*), (I), (II), and (III) react with aq. HNO₂ to form *p*-NO-derivatives. L. S. T.

Exchange experiments with trideuteroacetyl compounds. H. ERLÉNMEYER and H. SCHENKEL (Helv. Chim. Acta, 1938, 21, 706—708).—Trideutero-acetanilide (I) (90.3% pure) and AcCl (1:2) at 140° give the product CH₂.56D_{0.44}·COCl so that CD₃·CO in acetanilide/CD₃·CO in acetyl chloride = 1.77. Interchange is not observed when (I) is heated with OAc·C₆H₄·NHBz at 148°. H. W.

Mercuration of acetylurethane and its substituted amides. L. D. SHAH (J. Indian Chem. Soc., 1938, 15, 149—151).—(NAc·CO₂R)₂Hg are obtained from Hg acetamide and NHAc·CO₂R in H₂O or MeOH. The Hg derivatives of NHAc·CO·NHR are similarly prepared. The following are described: *Hg* acetylurethane, m.p. 174°, acetylphenylcarbamide, m.p. 205—206° (decomp.), acetyl-*m*-tolylcarbamide, m.p. 196—197° (from *N*-acetyl-*N'*-*m*-tolylcarbamide, m.p. 128°), acetyl-*o*-tolylcarbamide, m.p. 209—210°, acetyl-*p*-tolylcarbamide, m.p. 227—228° (decomp.), acetyl-α-naphthylcarbamide, m.p. 225—228° (decomp.), acetyl-β-naphthylcarbamide, m.p. 215—216° (decomp.), acetyl-*m*-4-xylylcarbamide, m.p. 231—232° (decomp.), acetyl-*p*-anisylcarbamide, m.p. 222° (decomp.) (from *N*-acetyl-*N'*-*p*-anisylcarbamide, m.p. 172—173°), and phenylurethane, m.p. 203°. The Hg derivatives with KI give K₂HgI₄ and the original ester (or carbamide); with N₂H₄ or NHPh·NH₂ Hg is liberated. A. L.

4-*p*-Aminobenzenesulphonamidobenzene-sulphonamides.—See B., 1938, 847.

Aromatic polysulphonamido-compounds.—See B., 1938, 764.

Electronic effect of the second nucleus on the behaviour of homonuclear naphthalene derivatives. H. H. HODGSON and R. L. ELLIOTT (J. Soc. Dyers and Col., 1938, 54, 264—268).—The reactions of substituents in one ring of C₁₀H₈ are influenced by the negative inductive effect of the other ring which *inter alia* reduces the basicity of NH₂ at 1 as compared with 2. Evidence for the existence of this effect, its electronic mechanism, and for the Erlenmeyer static formula for C₁₀H₈ is adduced from sundry experimental results, including (i) the preferential acetylation of β- as compared with α-C₁₀H₇·NH₂, (ii) the formation of a hydrochloride by 3:1- but a stannichloride by 1:3-C₁₀H₆Cl·NH₂ when the corresponding NO₂-compounds are reduced by SnCl₂; similarly hydrochlorides are formed by 1:2- and 1:4- but stannichlorides by 1:5- and 1:8-C₁₀H₆(NH₂)₂, as also by 2:4:1-NH₂·C₁₀H₅Cl·NHAc; (iii) monohydrochlorides are formed at 4 and 2, respectively, by 2:1:4- (I) and 4:1:2-C₁₀H₅Cl(NH₂)₂ (II) whilst (I) forms a di- but (II) a (2-)mono-acetyl derivative; (iv) HNO₂ interacts with 2:1:4-C₁₀H₅Cl(NH₂)₂ (III) tetrazotising 1 mol. which forthwith couples with (III) (2 mols.) eliminating Cl and yielding 2-chloro-1:4-bis-(1':4'-diamino-2'-naphthaleneazo)naphthalene; (v) a solid Na salt is formed by 4:2:1-NO₂·C₁₀H₅Cl·OH but with Br

or I at 2 no solid Na or K salts are formed, whereas 4-halogeno-2-nitro- α -naphthols form stable co-ordination compounds with Na, K, or Ag. The hydrolysis of 2:1- and 4:1- $\text{NO}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NHAc}$ by boiling aq. NaOH, the formation of dinaphthyls by Ullmann's reaction, and the coupling of 1:5- $\text{C}_{10}\text{H}_6(\text{OH})_2$ with diazo-compounds are similarly explained.

K. H. S.

Preparation of some cis-azo-compounds. A. H. COOK (J.C.S., 1938, 876—881).—Irradiation (Hg-vapour lamp) of a light petroleum solution of *trans*-azobenzene and selective adsorption on Al_2O_3 (both steps carried out in N_2) yields the *cis*-form (strongly adsorbed), reduced (Adams' catalyst) at the same rate as the *trans*-. *cis*-Benzeneazo-*p*-, m.p. 42—45°, and *cis*-*pp'*-azo-toluene, m.p. 105° (rapid heating), *cis*-*p*-benzeneazophenol Me and Et ethers (oils), and *cis*-*p*-chloroazobenzene (an oil), similarly obtained, are less stable than *cis*-azobenzene. The 4-OH-, -OAc-, -NH₂-, and -NHAc-derivatives of azobenzene show some separation during adsorption, but no *cis*-forms could be isolated. Benzeneazo- α -, α' -azo-, and $\beta\beta'$ -azo-naphthalene, *p*-cyanoazobenzene, and *oo'*- and *mm'*-azotoluene show no evidence of *cis*-forms. The last when irradiated in air gives a compound, $\text{C}_{14}\text{H}_{14}\text{ON}_2$, m.p. 59°, differing from any known azoxytoluene.

A. LI.

Action of *p*-toluenesulphonyl chloride on phenols containing azo-groups. A. B. SEN (Proc. Nat. Acad. Sci. India, 1937, 7, 218—221).—The *p*-toluenesulphonates (m.p. in parentheses) of the following are obtained when the hydroxyazobenzene is heated with *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2\text{Cl}$ and NPhEt_2 ; in no case was the phenolic OH replaced by Cl: 3-nitro-4-hydroxy- (112°), 5-bromo-3-nitro-4-hydroxy- (150°), 2'- (132°) and 4'-nitro-4-hydroxy- (167°), 2':4'-dinitro-4-hydroxy- (125°), 4'-nitro-4-hydroxy-3-methyl- (180°), 3-chloro- (178°) and 3-bromo-4'-nitro-4-hydroxy- (178°), 3-benzeneazo-4-hydroxy- (152°), 3:4'-dinitro-4-hydroxy- (157°), 3:5-dibromo-4'-nitro-4-hydroxy- (171°), 3:2'- (154°) and 3:3'-dinitro-4-hydroxy- (148°), 3-nitro-4-hydroxy-4'- (135°), -3'- (124°), and -2'-methyl- (134°), 2':4':6'-tribromo-3-nitro-4-hydroxy- (163°)-azobenzene. *s*-Trisbenzeneazophenol does not form an ester. Of the foregoing esters only the last eight (i.e., those containing NO_2 *ortho* to OH and also NO_2 or Me in the second ring) react with NH_2Ph in boiling EtOH-anhyd. NaOAc, the *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2\text{O}$ being replaced by NHPh . In this way the following were obtained: 3:4'-, m.p. 205°, 3:3'-, m.p. 180°, and 3:2'-, m.p. 166°, -*dinitro*-, 3:5-dibromo-4'-nitro- (?), m.p. 196°, 3-nitro-4'-, m.p. 138°, -3'-, m.p. 120°, and -2'-, m.p. 146°, -*methyl*-, and 2':4':6'-tribromo-3-nitro- (?), m.p. 154°, -4-anilinoazobenzene.

H. G. M.

Congo-red synthesis. E. R. KLINE (J. Chem. Educ., 1938, 15, 244).—A correction (cf. A., 1938, II, 229).

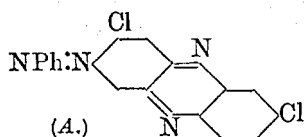
L. S. T.

1-Amino-2-naphthyl ethyl ether and its homologues as middle components in secondary bisazo-dyes. H. E. FIERZ-DAVID and H. ISCHER (Helv. Chim. Acta, 1938, 21, 664—706).—Dyes in which the group *o*-X·R·N·N·R'·Y-*o* (R and R' are substituted aromatic residues: X = OH, OMe, OEt, SO_3H , $\text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, NH_2 , Cl and Y = OH, NH_2) is present at least once, can be converted by treatment with Cr or Cu salts into complex compounds of the corresponding 2:2'-dihydroxyazo-dyes. 1-*o*-Methoxybenzeneazo- β -naphthol-6-sulphonic acid is thus converted by CuSO_4 and $\text{C}_5\text{H}_5\text{N}$ into the complex Cu compound of the 1-*o*-hydroxybenzeneazo-derivative, which is treated with Na_2S and then reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to *o*-OH· C_6H_4 · NH_2 and 1:2:6- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{SO}_3\text{H}$, showing thus that complex formation is accompanied by replacement of OMe by OH. Bisazo-dyes with 1:2- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OEt}$ (I) as intermediate component are unsuitable for analogous complex formation owing to their very great sensitivity towards acids and alkalis. Thus diazotised aniline-2:5-disulphonic acid (II) and (I) afford 1-(4-amino-3-ethoxy-1-naphthaleneazo)benzene-2:5-disulphonic acid (III), rapidly hydrolysed by alkali at 100° to NH_3 and a product, reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to (II) and 4-amino-2-ethoxy- α -naphthol [hydrochloride, m.p. 235° (decomp.); Bz_2 derivative, m.p. 186°]; in acid or neutral solution, also, NH_2 is replaced by OH. To determine the influence of SO_3H , dyes are prepared from (I) and sulphanilic and metanilic acid or NH_2Ph and it is shown that the effect is considerable but not of a fundamental nature. Examination of the dyes derived from (II) and α - $\text{C}_{10}\text{H}_7 \cdot \text{NH}_2$ (IV), 1:2- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OMe}$, 2:1- $\text{C}_{10}\text{H}_6\text{Me} \cdot \text{NH}_2$, and 3:1:4- $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OMe}$ and from 1:2- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{H} + p\text{-NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ shows that the dye from (IV) is stable towards hot acid or alkali. OMe has much the same action as OEt. Me causes marked loosening of NH_2 , the effect being somewhat less pronounced than that of Oalk. SO_3H appears to ensure complete stability. The 1-position in the C_{10}H_8 nucleus appears to have unique properties and not to be comparable with the corresponding C_6H_6 derivative. 1:2- $\text{NO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ is oxidised by HNO_3 to 1:2- $\text{NO}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, which is methylated (Me_2SO_4 on the Na salt in PhMe) and then reduced (Fe paste) to 1:2- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OMe}$, m.p. 54°, b.p. 110°/0.05 mm. Diazotisation of (III) requires unusual care and is best effected in solutions containing about 10% of NaCl; the products couple with β - $\text{C}_{10}\text{H}_7 \cdot \text{OH}$ (dye described), Schäffer salt, *R*-salt, or resorcinol in presence of $\text{C}_5\text{H}_5\text{N}$, $\text{NH}_3 + \text{EtOH}$, or Na_2CO_3 but not of NaOH. The bisazo-compounds are decomposed in acid or alkaline solution at 75°. In both cases the mol. is divided at the *sec.* N_2 group. Primary N_2 and OEt are largely unaffected. Degradation occurs with loss of N and re-formation of the terminal components through the stage of the mono-azo-dye of the two first components whereby OH replaces 1- NH_2 . Marked decomp. does not take place below 60°; at >75° this occurs also in presence of AcOH, NH_3 , and org. bases, e.g., $\text{C}_5\text{H}_5\text{N}$. A scheme of degradation is advanced. Decomp. is introduced by a hydrolysis and in its course resembles the conversion of ketonecarbazones into hydrocarbons (Wolff-Kishner). The bisazo-dye of this configuration behaves therefore like a readily hydrolysed carbazone. The prep. of 2:4-OH· $\text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{H}$ from 1:2:4- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{SO}_3\text{H}$ is described.

H. W.

L** (A., II.)

Azo-dyes and their intermediates. XX. Polyazobenzenes. P. RUGGLI and C. PETITJEAN (Helv. Chim. Acta, 1938, **21**, 711—732).—*p*-(Benzeneazo)azobenzene (I), m.p. 167°, obtained in 87% yield from PhNO and $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot p$ in AcOH, when hydrogenated (Raney Ni in dioxan at 70°) and then acetylated affords *p*- α - or - β -acetyl- β -phenylhydrazinoazobenzene, m.p. 185°, which when further hydrogenated gives $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, NH_2Ph , $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$, and NHPhAc . When boiled with acids in contact with air it is not hydrolysed but converted into (I), whereas boiling NaOH-EtOH in N_2 transforms it into *p*-phenylhydrazinoazobenzene, which is converted by



HCl into a substance, m.p. 263—264° (probably A), the filtrate from which gives a Bz derivative, $\text{C}_{25}\text{H}_{20}\text{ON}_4$, m.p. 208°.

4:4'-Di(benzeneazo)azobenzene, m.p. 232—233°, is readily obtained from ($p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}$)₂ and PhNO in AcOH. NH_2Ph and $p\text{-C}_6\text{H}_4(\text{NO})_2$ in warm EtOH containing a little AcOH yield *p*-(benzeneazo)azoxybenzene, $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{NPh}$, m.p. 134°, which when completely hydrogenated and acetylated gives NHPhAc and $p\text{-C}_6\text{H}_4(\text{NHAc})_2$ and when partly hydrogenated yields (I), also obtained by use of Zn dust and alkali. $p\text{-C}_6\text{H}_4(\text{NO})_2$ and $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ yield 4-bromo-4'-(*p*-bromobenzeneazo)azoxybenzene, m.p. 246°, reduced (Raney Ni in $\text{C}_5\text{H}_5\text{N}$) to 4-bromo-4'-(*p*-bromobenzeneazo)benzene, m.p. 274°. Analogously $p\text{-C}_6\text{H}_4(\text{NO})_2$ and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHAc}$ afford 4-acetamido-4'-(*p*-acetamidobenzeneazo)azoxybenzene (II), $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, m.p. 317°, hydrolysed by N-KOH -EtOH to the corresponding diamine (III), m.p. 246—247° [*Bz*₂ derivative, m.p. 328°; (CHPh)₂ compound, m.p. 209°]. (III) and PhNO or $p\text{-C}_6\text{H}_4(\text{NO})_2$ and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$ yield 4-benzeneazo-4'-(*p*-benzeneazobenzeneazo)-azoxybenzene $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NPh}$, m.p. 257°, contaminated with the -azobenzene, $\text{C}_6\text{H}_4(\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NPh})_2$ (IV). Hydrogenation (Raney Ni in $\text{C}_5\text{H}_5\text{N}$ at room temp.) of (III) and treatment of the product with boiling Ac_2O under N_2 gives 4-acetamido-4'-(*p*-acetamidobenzeneazo)azobenzene, m.p. 325° (corresponding *Bz*₂ derivative, m.p. 336°), hydrolysed (1.4*N*-NaOH) to 4-amino-4'-(*p*-aminobenzeneazo)azobenzene, m.p. 256—257°. This base with an excess of PhNO in boiling AcOH yields (IV), m.p. 275°. $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot p$ (V) and $p\text{-C}_6\text{H}_4(\text{NO})_2$ afford the substance, $p\text{-C}_6\text{H}_4(\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc})_2$, amorphous, decomp. 290—300°, hydrolysed by alkali to the corresponding diamine, m.p. 292°, which with PhNO yields a substance, $\text{C}_{42}\text{H}_{30}\text{N}_{12}$. $p\text{-C}_6\text{H}_4(\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot p)_2$ and Ac_2O in cold $\text{C}_5\text{H}_5\text{N}$ yield 4-amino-4'-(*p*-acetamidobenzeneazo)azobenzene, m.p. 271—272°, which does not appear to condense with $p\text{-C}_6\text{H}_4(\text{NO})_2$. (V) and 30% H_2O_2 in AcOH yield a mixture (VI), m.p. 333—335° (decomp.), of ($\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$)₂ and (II), hydrolysed to a mixture of the bases, m.p. 263°. Catalytic hydrogenation of (VI) yields homogeneous 4:4'-di-(*p*-acetamidobenzeneazo)azobenzene, m.p. 345—348° (decomp.), hydrolysed to the diamine, m.p. (indef.) 280—283°. H. W.

Diazo-chemistry. Tetrazotisation of *o*-phenylenediamine. H. A. J. SCHOUTISSEN (Rec. trav. chim., 1938, **57**, 710—718).—The tetrazotisation of phenylenediamines is reviewed. The following is new. $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ is tetrazotised by $\text{NO}\cdot\text{HSO}_4$ in H_3PO_4 or AcOH, freed from excess of HNO_2 , and coupled with 1 mol. of PhOH (in AcOH), thus giving a cryst. product (I), which explodes when heated, and is reduced by abs. EtOH at 100° to $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$. Coupling with PhOMe or PhOEt results in loss of Me or Et and gives (I); $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ (1 mol.) gives a product, reduced by EtOH to 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\text{Ph}$. SnCl_2 -reduction of tetrazotised $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives only $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$. The above mono-couplings show the existence of $o\text{-N}_2\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NX}$ in strong acid. In dil. acid the second N_2X couples. R. S. C.

Adsorption of diazo-compounds on cadmium and magnesium hydroxides. III. Purification of nitrodiazoamino-compounds. F. P. DWYER (J. Proc. Austral. Chem. Inst., 1938, **5**, 67—77).—Nitro- and dinitro-diazoamino-compounds are obtained pure by dissolving in aq. MeOH and adsorption of the impurities (diazoaminoazo-compounds) on $\text{Cd}(\text{OH})_2$. Compounds having NO_2 at 2 and/or 4 afford intense colours when dissolved in alcoholic alkali; with NO_2 at 3 the colour is weak. The m.p. of 17 purified compounds are recorded: 2-, m.p. 105—106°, 3-, m.p. 132°, and 4-, m.p. 151°, -nitro-; 2:2'-, m.p. 199°, 2:3'-, m.p. 173—174°, 2:4'-, m.p. 193—194°, 3:3'-, m.p. 197—198°, 3:4'-, m.p. 226°, and 4:4'-, m.p. 227°, -dinitro-; 2-nitro-3'-, m.p. 120°, and 4'-, m.p. 113—114°, 3-nitro-2'-, m.p. 114°, 3'-, m.p. 115°, and 4'-, m.p. 108°, and 4-nitro-2'-, m.p. 146—147°, 3'-, m.p. 149°, and 4'-, m.p. 160°, -methyl-benzenediazoaminobenzene. K. H. S.

Iodometric determination of phenol. B. G. ŠIMEK and S. POLÁTSKÝ (Mitt. Kohlenforschungsinstit. Prag, 1937, **3**, 204—217).—Reaction between PhOH and I in the presence of borax leads to the formation of complex mixtures having no definite stoichiometric composition; it cannot be used as the basis of a method of determining PhOH. A. B. M.

Crystalline products of the initial reaction in the formation of phenol plastics. H. STÄGER and J. BRERT (Helv. Chim. Acta, 1938, **21**, 641—650).—Trihydric phenolic alcohols are not formed during the production of phenol plastics in alkaline solution. Oily or resinous condensation products are obtained from PhOH, CH_2O , and NaOH or $\text{Ca}(\text{OH})_2$ in the mol. ratio 1:3:1. From PhOH, CH_2O , and NH_3 (1:3:0.8) cryst. hexamethylenetriphenol is isolated. Molar mixtures of PhOH and alkali with a slight excess of CH_2O afford *o*- and *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$. *m*- or *p*-Cresol, CH_2O , and NaOH (1:1:1) do not give cryst. products but merely resinous mixtures; if the ratio is 1:2:1 the corresponding hydroxytoluyl alcohols are obtained cryst. Acid (HCl) condensation of PhOH and CH_2O (1:1 or 2:1) gives derivatives of dihydroxydiphenylmethane. PhOH, CH_2O , and NaOH (1:1.4:1.2) give *o*- and *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$, whereas $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{OH}\cdot p)_2$ results when the ratio is 1:1:0.2. It is therefore possible under suitable conditions for

the same primary cryst. products to result in acid and in alkaline solution. The following courses of action are probable: $R\cdot OH + CH_2O \rightarrow OH\cdot R'\cdot CH_2\cdot OH$ (I); $R\cdot OH + xCH_2O \rightarrow OH\cdot R'\cdot (CH_2\cdot OH)_x$; (I) + $R\cdot OH \rightarrow H_2O + OH\cdot R'\cdot CH_2\cdot R'\cdot OH$ (II); (II) + $CH_2O \rightarrow OH\cdot R'\cdot CH_2\cdot R''(OH)\cdot CH_2\cdot OH$ (III); (III) + $R\cdot OH \rightarrow OH\cdot R'\cdot CH_2\cdot R''(OH)\cdot CH_2\cdot R'\cdot OH$ or, in general, $xR\cdot OH + (x-1)CH_2O \rightarrow OH\cdot R'\cdot CH_2\cdot R''(OH\cdot CH_2)_{x-2}\cdot R'\cdot OH + (x-1)H_2O$. The second stage is doubtful.

H. W.

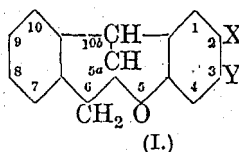
Properties and uses of pentachlorophenol. T. S. CARSWELL and H. K. NASON (Ind. Eng. Chem., 1938, 30, 622—626).— $C_6Cl_5\cdot OH$, m.p. 190.2°, in dil. aq. EtOH can be titrated with standard NaOH to thymol-blue; 1, 5, and 25% aq. solutions of the Na salt have p_H approx. 8.0, 9.6, and 10.5, respectively. The phenol is stable to heat and boiling H_2O or dil. acids. It yields coloured Cu, Ag, and Hg salts. Data for solubility and v.p. are given. The min. lethal dose (Na salt) intravenously in rabbits and guinea-pigs is approx. 36 mg., and subcutaneously 60 mg., per kg.; the toxæmia produced is accompanied by fever, hyperglycæmia, glycosuria, and circulatory failure. Comparative data for its fungicidal properties are tabulated and its use for preserving timber etc. is discussed. F. O. H.

Ozonisation of anethole, estragole, and ψ -estragole. Properties of ozonides. E. BRINER and S. DE NEMITZ (Helv. Chim. Acta, 1938, 21, 748—671).—Ozonisation of $p\text{-OMe}\cdot C_6H_4\cdot CH\cdot CHMe$ (I) occurs more regularly and with less production of resinous products than does that of $p\text{-OMe}\cdot C_6H_4\cdot CH_2\cdot CH\cdot CH_2$ or $p\text{-OMe}\cdot C_6H_4\cdot CMe\cdot CH_2$. Spontaneous scission of the ozonide of (I) gives $p\text{-OMe}\cdot C_6H_4\cdot CO_2H$ and $MeCHO$, whereas in the presence of H_2O the products are $OMe\cdot C_6H_4\cdot CHO$ and $AcOH$ and reductive fission affords the two aldehydes. The action of reducing agents (KI, $NaHSO_3$) proves that the ozonide exercises a peroxidising action equal to that of the absorbed O_3 . The constitution of ozonides is discussed. H. W.

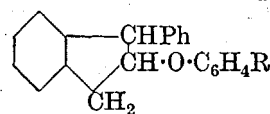
Preparation of N-monomethylated derivatives of aminophenols. M. MORREN (Congr. Chim. ind. Bruxelles, 1935, 15, I, 383—386; Chem. Zentr., 1936, ii, 1909).— $p\text{-NH}_2\cdot C_6H_4\cdot OH$ (I) is N-methylated (yield 70%) by first converting into $OH\cdot C_6H_4\cdot NH\cdot CN$ [from (I) and $CNCl$ in aq. $NaOAc$ at 20°], methylating this (Me_2SO_4 ; 10% $NaOH$), and hydrolysing the $p\text{-OH}\cdot C_6H_4\cdot NMe\cdot CN$ with boiling 20% H_2SO_4 . $p\text{-OH}\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2$ is methylated (Me_2SO_4) to $p\text{-OMe}\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2$. A. H. C.

Reaction of indene dichloride with phenols. C. M. SUTER and G. A. LUTZ (J. Amer. Chem. Soc., 1938, 60, 1365—1368).—Indene dichloride and $p\text{-C}_6H_4Cl\cdot OH$ at 150—170° give 2 HCl, 2-chloro-5a:10b-dihydro 6-benz(b)indeno[1:2-d]furan [(I); $X=Cl$; $Y=H$], m.p. 114—115°, b.p. 185—185°/4 mm. (unaffected by HI or $KMnO_4$), 3,5'-chloro-2'-hydroxyphenylindene, b.p. 180—190°/4 mm. (benzoate, m.p. 139—140°), and 1:1-di-(5'-chloro-2'-hydroxyphenyl)indane, b.p. 257—262°/4 mm. m-Cresol gives the ether [(I); $X=H$; $Y=Me$], b.p. 170—175°/4 mm., m.p. 131.5—132.5° (with Br gives HBr and a substance, $C_{16}H_{12}OBr_2$, m.p. 234.5—235°), impure hydroxy-

m-tolylindene, b.p. 175—185°/4 mm., and 1:1-dihydroxy-m-tolylindene, b.p. 250—255°/4 mm. p-Cresol gives the ether [(I); $X=Me$; $Y=H$], b.p.



(I.)



(II.)

189—195°/4 mm., m.p. 85—86°, hydroxy-p-tolylindene, and 1:1-dihydroxy-p-tolylindene, b.p. 250—255°/4 mm. PhOH gives the ether [(I); $X=Y=H$], m.p. 78.5—79°, b.p. 165—175°/4 mm. [Br_2 -derivative, m.p. 195—196° (decomp.)], dihydroxydiphenylindanes (?), m.p. 224—225° (Me ether, m.p. 208—210°; also obtained in boiling PhBr in 8% yield), and (mostly) b.p. 250—255°/4 mm. [derived di(aryloxyacetic acid) (Ag_2 salt); the Me_2 ether, b.p. 200—210°/3 mm., with C_6H_6 and $AlCl_3$ gives PhOMe and (?) 3-phenylindene]. Ethers (I) with C_6H_6 and $AlCl_3$ give 3-phenylindene and the appropriate phenol, probably by way of (II); e.g., (I) ($X=Me$; $Y=H$) gives p-cresol. M.p. are corr. R. S. C.

Cyclic acetals from diacetyl and pyrocatechol. J. J. VAN DER SPEK (Rec. trav. chim., 1938, 57, 677—680).—The cryst. product obtained from Ac_2 and $o\text{-C}_6H_4(OH)_2$ (van der Spek, Diss., Delft, 1938) is $o\text{-C}_6H_4\langle\begin{smallmatrix} CO\cdot CR\cdot O \\ CO\cdot CR\cdot O \end{smallmatrix}\rangle C_6H_4\text{-}o$ (I) ($R=Me$) and not, as pre-

viously supposed, the substance, $[o\text{-C}_6H_4\langle\begin{smallmatrix} O \\ O \end{smallmatrix}\rangle CMe]_2$, which is obtained (m.p. 127—128°) by condensing $o\text{-C}_6H_4(OH)_2$ with $COMe\cdot CHMe\cdot OAc$ to give $o\text{-C}_6H_4\langle\begin{smallmatrix} O \\ O \end{smallmatrix}\rangle CMe\cdot CHMe\cdot OAc$, which is then hydrolysed, oxidised, and finally condensed further with $o\text{-C}_6H_4(OH)_2$. Similarly, the product, m.p. 159°, obtained from $o\text{-C}_6H_4(OH)_2$ and $(CHO)_2$ is (I) ($R=H$). Both compounds (I) have the same dipole moment (1.26), and hence a cis-structure. R. S. C.

Constituents of natural phenolic resins. XI. Synthesis of 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-2- and -3-methylnaphthalenes. R. D. HAWORTH and D. WOODCOCK (J.C.S., 1938, 809—813).—The lactone of 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid (A., 1935, 860; 1936, 80) is reduced ($Na\text{-Hg}$ in boiling KOH) to one, m.p. 180°, of the four possible racemates of conidendrin Me_2 ether (loc. cit.), since it is oxidised by $NaOBr$ to a mixture of a lactone, $C_{22}H_{24}O_7$, m.p. 205—206°, 2-veratroylveratric acid, and (?) 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-1:2:3:4-tetrahydroxynaphthalene-2:3-dicarboxylic acid (Me_2 ester, m.p. 148—149°), and (abnormally) by $Pb(OAc)_4$ in $AcOH$ to 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-2-methylnaphthalene (I), m.p. 141°, also synthesised as follows: 3:4-(OMe) $_2C_6H_3\cdot COEt$ (from veratrole, $EtCOCl$, and $AlCl_3$ in $PhNO_2$) with Br in $CHCl_3$ yields α -bromo- α -veratroylethane, m.p. 83—84°, which when treated with $CHNa(CO_2Et)_2$ in C_6H_6 and the product hydrolysed and heated to 180° affords β -veratroyl-n-butyric acid, m.p. 129°. The Na salt of this with veratraldehyde and Ac_2O yields the lactone m.p.

183°, of β -veratroyl- α -veratrylidene-*n*-butyric acid. The crude acid with CH_2N_2 followed by MeOH-HCl affords the *Me* ester, m.p. 178°, of 6 : 7-dimethoxy-1-(3' : 4'-dimethoxyphenyl)-2-methylnaphthalene-3-carboxylic acid, m.p. 232°, which gives (I) with Cu and quinoline. The chloride, m.p. 183—184°, of 6 : 7-dimethoxy-1-(3' : 4'-dimethoxyphenyl)naphthalene-3-carboxylic acid (II) (A., 1935, 860) is reduced (Pd-BaSO_4 in xylene) to the 3-aldehyde, m.p. 163—164° (oxime, m.p. 185°), the hydrazone, m.p. 175—176°, resolidifying with m.p. 305—306°, or semicarbazone, m.p. 223—224°, resolidifying with m.p. 308—309°, of which on reduction (NaOEt) and remethylation (CH_2N_2) gives 6 : 7-dimethoxy-1-(3' : 4'-dimethoxyphenyl)-3-methylnaphthalene (cf. A., 1937, II, 498) (picrate, m.p. 133°).

6 : 7-Dimethoxy-1-(3' : 4'-dimethoxyphenyl)-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid, m.p. 220—222°, is synthesised from $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ and veratrole, by treating with conc. $\text{H}_2\text{SO}_4\text{-AcOH}$, followed by boiling AcCl , then AlCl_3 in PhNO_2 at 0°, and reducing the product with Zn-Hg and HCl . Reduction (Na-Hg in boiling KOH) of (II) yields 1 : 2 : 3 : 4-tetrahydronaphthalene-3-carboxylic acid, m.p. 170° (monohydrate, m.p. 133°; *Me* ester, m.p. 143—144°).

A. LI.

Aromatic hydroxy-sulphones. M. E. HEPPENSTALL and S. SMILES (J.C.S., 1938, 899—905).—Na salts of *o*-OH-sulphones may be obtained in the covalent state, a fact consistent with the rearrangement of OH-sulphones to ether sulphinic acids (A., 1934, 647). They are decomposed by $\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, are readily methylated in cold aq. solution, and react normally with 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$. The following sulphones have been prepared : substituted diphenylsulphones : 2-hydroxy-, m.p. 97° [monohydrate, m.p. 82°; *Me* ether, m.p. 143°; *Ac*, m.p. 84°, and *Na* derivative, m.p. 290—293° (more sol. in cold CHCl_3 than in hot)]; 3-hydroxy-, m.p. 163° (from 3-nitro-*via* 3-amino-, m.p. 117°) (*Me* ether, m.p. 90-5°); 4-hydroxy- (from 4-nitro-) (monohydrate); 2-methoxy-5-methyl-, m.p. 140° (from 2 : 5- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_2\text{Cl}$, C_6H_6 , and AlCl_3), hydrolysed (HBr) to the phenol, m.p. 139° (monohydrate; *Na* derivative, m.p. 260°, sol. in warm CHCl_3); 5-chloro-2-methoxy-, m.p. 144° (from 2 : 5- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{SO}_2\text{Cl}$, C_6H_6 , and AlCl_3), hydrolysed to the phenol, m.p. 139° {*Ac*, m.p. 134°, and *Na* derivative, m.p. 247°; 2 : 4-dinitrophenyl ether, m.p. 187° [from the latter and 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ in hot EtOH]; *Li* derivative (*di*-hydrate, m.p. 198°)}; 2 : 2'-dihydroxy-5 : 5'-dimethyl- (*Ac*₂, m.p. 211°, and *Na* derivative, m.p. 190°); and 2-hydroxy-2'-methoxy-5 : 5'-dimethyl-, m.p. 153° (from 1 : 4 : 2- $\text{CO}_2\text{Et}\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_2\text{Cl}$, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$, and AlCl_3 , and hydrolysis of the product with EtOH-NaOH) [*Na*, m.p. 219° (sol. in CHCl_3), and *Li* derivative]; phenylmethylsulphones : 2-methoxy-, m.p. 95° (by methylating *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$), hydrolysed (HBr) to 2-hydroxy-, m.p. (almost anhyd.) 67° (monohydrate, m.p. 87-5°); 3-amino-, m.p. 58° (from 3- NO_2 -compound, *Sn*, and HCl); 3-hydroxy-, m.p. 82° (from 3- NH_2 -compound) (*Me* ether, m.p. 47°, also obtained from *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$); 4-methoxy-, m.p. 121° (from *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{H}$), hydrolysed to 4-

hydroxy-, m.p. 94° (monohydrate, m.p. 49°); 2-hydroxy-5-methyl-, m.p. 89° (from the *Me* ether and HBr) (monohydrate, m.p. 78°); and 5-chloro-2-hydroxy-, m.p. 140° (from the *Me* ether). Reduction (Na_2SO_3) of 1 : 2 : 4- $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{SO}_2\text{Cl})_2$ and treatment of the *K* salt of the product with MeI affords 2 : 4-bismethylsulphonylanisole, m.p. 197°, hydrolysed to the phenol (poor yield), m.p. 220°, better prepared as follows : *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\text{Me}$ with ClSO_3H at 170° yields 1-chloro-2-chlorosulphonyl-4-methylsulphonylbenzene, m.p. 144° (anilide, m.p. 161°); this, either by treatment with $\text{CHNa}(\text{CO}_2\text{Et})_2$ and then MeI , or by reduction (HI in AcOH) to di-2-chloro-5-methylsulphonylphenyl disulphide, m.p. 253°, further reduction (glucose) and methylation (Me_2SO_4) to 1-chloro-4-methylsulphonyl-2-methylthiolbenzene, m.p. 107°, and oxidation (H_2O_2) of this, yields 1-chloro-2 : 4-bismethylsulphonylbenzene, m.p. 187°. This is readily hydrolysed to the phenol, reacts with NaOEt in boiling EtOH at about the same rate as 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$, giving the *Et* ether, m.p. 201°, and yields with NH_2Ph , 2 : 4-bismethylsulphonyldiphenylamine, m.p. 218°, with piperidine, *N*-2' : 4'-bismethylsulphonylphenylpiperidine, m.p. 156°, with NaSPh in boiling EtOH , 2 : 4-bismethylsulphonyldiphenyl sulphide, m.p. 232°, and with PhSO_2Na in boiling $(\text{CH}_2\cdot\text{OH})_2$, the sulphone, m.p. 270—271°, also obtained by oxidising the sulphide with H_2O_2 in AcOH .

A. LI.

Preparation of benzyloxyalkyl *p*-toluenesulphonates. C. L. BUTLER, (MISSES) A. G. RENFREW, and M. CLAPP (J. Amer. Chem. Soc., 1938, 60, 1472—1473).—The glycol (5 mols.), CH_2PhCl (2 mols.), and 85% KOH (2 mols.) at 90—130° give 66—72% yields of ethylene, b.p. 131°/13 mm., propylene, b.p. 128°/12 mm., and trimethylene glycol CH_2Ph ether, b.p. 142°/10 mm., which with *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ and $\text{C}_5\text{H}_5\text{N}$ afford β -benzyloxyethyl, m.p. 45°, β -benzyloxyiso-, m.p. 49°, and γ -benzyloxy-*n*-propyl *p*-toluenesulphonate, m.p. 37°, respectively. Glycerol $\alpha\gamma$ -(CH_2Ph)₂ ether β -*p*-toluenesulphonate, amorphous, is also prepared.

R. S. C.

Stereoisomerism of cyclohexanediols. II. Preparation and properties of the 1 : 4-cyclohexanediols. J. COOPS, J. W. DIENSKE, and W. M. SMT (Rec. trav. chim., 1938, 57, 637—642; cf. A., 1938, II, 184).—Passage of dry HCl into *cis*-cyclohexane-1 : 4-diol (CPh_3)₂ ether in C_6H_6 gives a syrupy compound of the free diol, 1HCl, and $\alpha\text{C}_6\text{H}_5$, soon passing into a cryst. compound, 4diol, 2HCl, C_6H_6 , which in a vac. gives the free diol. The *trans*-ether gives similarly a very unstable, solid compound, 5 diol + $\frac{1}{2}$ 2HCl, passing rapidly into the free diol. Both diols have the properties previously reported (*loc. cit.*). The *cis*-diol is shown to give liquid crystals at 101.4° and a normal liquid at 113°, the first change requiring 4 times as much heat as does the second.

R. S. C.

Stereo-chemistry of seven-membered carbon rings. P. H. HERMANS and C. J. MAAN (Rec. trav. chim., 1938, 57, 643—652).—According to Stuart models, *trans*-cycloheptane-1 : 2-diol in a form suitable for ring-formation with H_3BO_3 occurs in the statistically preferred configurations of the "chair" form. This is, however, not the case for the *cis*-diol

in either the "boat" or the "chair" form. Yet both diols form rings with H_3BO_3 . Connexion of potential energy of the mol. with considerations of the probability of forms and of chemical reactions thus appears invalid.

R. S. C.

Phenanthrene series. XVI. Amino-alcohols and miscellaneous derivatives of phenanthrene. J. VAN DE KAMP, A. BURGER, and E. MOSETTIG (J. Amer. Chem. Soc., 1938, 60, 1321—1325; cf. A., 1937, II, 423).—The following are prepared: 3-, m.p. 120.5—121°, and 9-phenanthrodimethylamide, m.p. 182.5—183°. β -Dimethylaminoethyl 3-, m.p. 202—202.5°, and 9-phenanthroate hydrochloride (from the acid chloride and $NMe_2 \cdot [CH_2]_2 \cdot OH$ in $CHCl_3$), m.p. 171—171.5° (corresponding *picrates*, m.p. 177.5—178° and 144—145°, respectively). 9-Aminomethylphenanthrene [by hydrogenation (slow; PtO_2) of the 9-CN-derivative in $AcOH$], m.p. 108—108.5° [hydrochloride, m.p. 292—294° (decomp.)]. 3-Oximinoacetylphenanthrene (by $BuNO_2$; 40—45% yield), m.p. 272—273°, which with $SnCl_2 \cdot HCl \cdot EtOH$ gives 3-glycylphenanthrene hydrochloride, m.p. 260—320° (decomp.) [corresponding *picrate*, m.p. 193° (decomp.)], hydrogenated (PtO_2) in $EtOH$ to 3- β -amino- α -hydroxyethylphenanthrene, m.p. 139—139.5° [hydrochloride, m.p. 235—236° (decomp.)]; *picrate*, m.p. 218.5—219.5°. 2-Oximinoacetylphenanthrene (by $C_5H_{11}NO_2$; 30% yield), m.p. 175—176° (decomp.). 2-Glycyl- [hydrochloride, m.p. 280—310° (decomp.)]; *picrate*, m.p. 185—189° (decomp.)], and 2- β -amino- α -hydroxyethylphenanthrene, m.p. 143—144° [hydrochloride, m.p. 251—254° (decomp.)]; *picrate*, m.p. 205—206° (decomp.)]. 3- β -Diethylamino- α -acetoxylethylphenanthrene hydrochloride, m.p. 221—221.5°. 3-1':2':3':4'-Tetrahydroisquinolino-4-hydroxy-1:2:3:4-tetrahydrophenanthrene, m.p. 125—126° {acetate, m.p. 118—122°; *Ac* derivative, m.p. 123—125° [hydrochloride, m.p. 200—201° (decomp.)]}. 3-Hydroxy-6- β -diethylamino- α -hydroxyethylphenanthrene (prep. from 6- β -diethylaminoacetyl-3-acetoxypheanthrene perchlorate by H_2 - PtO_2 in $MeOH$ and subsequent hydrolysis), m.p. 124.5—125.5°, with Ac_2O - C_5H_5N at room temp. gives the 6- β -diethylamino- α -acetoxylethyl derivative (I) (20—30% yield) (hydrochloride, m.p. 199—201°), and with hot Ac_2O - $NaOAc$ gives the 3-*Ac* derivative of (I) (hydrochloride, m.p. 201—202°). 3-1':2':3':4'-Tetrahydroisquinolinoacetylphenanthrene hydrochloride (from 3-bromoacetylphenanthrene and tetrahydroisquinoline at room temp.), m.p. 246—248° (decomp.), converted by H_2 - PtO_2 in 80% $MeOH$ into 3- β -1':2':3':4'-tetrahydroisquinolino- α -hydroxyethylphenanthrene hydrochloride, m.p. 198—199° (decomp.) (corresponding *picrate*, m.p. 180—181.5°). 3-Acetoxy-(? 7 or 8)-acetylphenanthrene (obtained in 1% yield as a by-product from 3-acetoxypheanthrene, $AcCl$, and $AlCl_3$), m.p. 124—125°, and thence the 3-*OH*-, m.p. 237—238°, and 3-*OMe*-derivative, m.p. 93—94°, 3-methoxy-, m.p. 220—223° (decomp.) (*Me* ester, m.p. 127.5—128°), and 3-hydroxy-phenanthrene-(? 7- or 8)-carboxylic acid, m.p. 281—284° (decomp.). β -2-, m.p. 164—165°, and β -3-Phenanthrylpropionhydrazide, m.p. 189—190°, and β -3-phenanthrylpropionamide, m.p. 161.5—162° (all prepared from the esters). β -1:2:3:4:5:6:7:8-

Octahydro-9-phenanthrolylpropionic acid [from octahydrophenanthrene, $(CH_2 \cdot CO)_2O$, and $AlCl_3$ in CS_2], m.p. 143—144°, reduced (Clemmensen) to γ -1:2:3:4:5:6:7:8-octahydro-9-phenanthrylbutyric acid, m.p. 128—129°, which with 75% (vol.) H_2SO_4 at 100° gives 4-ketododecahydrotriphenylene, m.p. 222—222.5°, reduced to dodecahydrotriphenylene and obtained therefrom by CrO_3 in 80% $AcOH$. β -Phenanthrylethylamines are obtained by electrolytic reduction of β -nitro- α -phenanthrylethylenes. Conversion of phenanthraldehydes into the acrylic and propionic acids and subsequent Curtius degradation give good yields, except of the urethanes.

R. S. C.

Structure and absorption [spectra] of basic triphenylmethane dyes. (MME.) RAMART-LUCAS (Compt. rend., 1938, 206, 1656—1659; cf. A., 1938, II, 110).—The change in absorption when the salts are changed to free base is small and the degree of ionisation has little effect on the colour. The bases and some of their derivatives exist in solution in two forms in equilibrium; the colourless form probably has the same structure as the leuco-base (cf. A., 1928, 627) whereas the coloured form has Nietzki and Armstrong's quinonoid structure. Spectroscopic measurements show that the proportions of the colourless and coloured forms present depend on the nature of the dye, the solvent, p_H , and the λ of light. In $EtOH$, fuchsin and crystal-violet bases are almost entirely quinonoid, but alkali changes them to the colourless forms.

J. L. D.

Cholesterol. XIV. isoCholesterol, m.p. 141—143°, and **epicholesterol**. R. DE FAZI (Ann. Chim. Farm., 1938, 1, 38—42).—The epicholesterol, m.p. 141°, of Marker *et al.* (A., 1936, 604) is considered identical with the author's isocholesterol, m.p. 141—143° (A., 1933, 710). Structures of the two chlorodihydrocholesterols, m.p. 126—127°, and 136—138°, are discussed.

E. W. W.

Oxidation of the trianhydrolactone of ouabain, and of epineoergosterol. P. N. CHAKRAVORTY and E. S. WALLIS (J. Amer. Chem. Soc., 1938, 60, 1379—1381).—Fieser and Newman's formula (A., 1936, 1116) for the trianhydrolactone from ouabain is untenable, since the acetate with CrO_3 gives no ketone and with HNO_3 gives no aromatic acid. *epi*Neoergosterol has m.p. 175—176°; its acetate, m.p. 98°, with CrO_3 - $AcOH$ at 60—65° gives a ketone, $C_{18}H_{26}O$, m.p. 114—115° [semicarbazone, m.p. 255° (decomp.)], the absorption of which resembles that of neoergopentane (cf. Marker *et al.*, A., 1936, 1256; Windaus *et al.*, A., 1937, II, 99).

R. S. C.

Sterol group. XXXVII. Structure of lumisterol and its stereoisomerides. I. M. HEILBRON, T. KENNEDY, F. S. SPRING, and G. SWAIN (J.C.S., 1938, 869—876).—Reduction [$Al(OPr^i)_3 + Pr^iOH$] of ergostatrienone yields a complex, m.p. 196°, spectroscopically identical with ergosterol, which after keeping has m.p. 155° and a much decreased light absorption. Resolution before or after with digitonin gives ergosterol and a trienol, m.p. 152° (cf. Marker *et al.*, A., 1937, II, 496) [formed by isomerisation of the unstable, intermediate *epi*ergosterol (cf. Windaus and Buchholz, A., 1938, II, 186)], which with Ac_2O and

NaOAc gives *ergostatetraene*, m.p. 104°, $[\alpha]_D^{20}$ -40.5° in CHCl_3 . Oxidation $[\text{Al}(\text{O}i\text{Bu})_3]$ in COMe_2 of lumisterol gives *lumistatrienone*, m.p. 139–140°, $[\alpha]_D^{20}$ +48.7° in CHCl_3 [*semicarbazone*, m.p. 247° (decomp.); *enol-acetate*, m.p. 98°, $[\alpha]_D^{20}$ +293.7° in CHCl_3], reduced to a complex, m.p. 159.5°, of lumisterol with *epilumisterol*, m.p. 109–110°, $[\alpha]_D^{20}$ +224.6° in CHCl_3 (*acetate*, m.p. 114–115°, $[\alpha]_D^{20}$ +175° in CHCl_3). Oxidation of dehydroergosterol yields *ergostatetraenone*, m.p. 140–142°, $[\alpha]_D^{20}$ +190° in CHCl_3 [*semicarbazone*, m.p. 224° (decomp.); *enol-acetate*, m.p. 161°, $[\alpha]_D^{20}$ -232.5° in CHCl_3], reduced to a complex of dehydro- and (unstable) *epidehydro-ergosterol*. That *epi ergo-* differs from *lumi-sterol* and *pyrocalleiferol*, and *epilumi-* from *ergo-sterol* and *isopyrocalleiferol* substantiates the structures assumed by Windaus and Dimroth (A., 1937, II, 147). *Ergostatrienone enol-acetate* ($\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$), m.p. 146°, $[\alpha]_D^{20}$ -143.5° in CHCl_3 , is hydrolysed ($\text{MeOH}-\text{KOH}$) to *isorgostatrienone* (A., 1937, II, 417) (*enol-acetate*, m.p. 137°, $[\alpha]_D^{20}$ -84.6° in CHCl_3). A. Li.

Chemical investigation of the roots of *Hemidesmus indicus*. I. A. T. DUTTA, S. GHOSH, and R. N. CHOUPRA (Arch. Pharm., 1938, 276, 333–340).—The roots contain 0.225% (on dry wt.) of an essential oil [80% of which is 2 : 4 : 1- $\text{OH}:\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO}$ (*oxime*, m.p. 141°; *semicarbazone*, m.p. 224°), responsible for the typical odour], two sterols, *hemidosterol*, $\text{C}_{34}\text{H}_{60}\text{O}$, m.p. 182.4°, $[\alpha]_D^{30}$ +83° in CHCl_3 (*Ac*, m.p. 198°, and *Bz* derivative, m.p. 188.5°), and *hemidesmol*, $\text{C}_{33}\text{H}_{58}\text{O}$, m.p. 161°, $[\alpha]_D^{30}$ +57° in CHCl_3 (*Ac*, m.p. 188°, and *Bz* derivative, m.p. 222.5°), sugars, resins, tannins, and a small amount of a glucoside, m.p. 133–136° (decomp.).

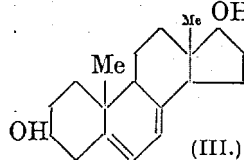
R. S. C.

Preparation and reactions of mono- and dihydroxycholestanes. I. M. HEILBRON, W. SHAW, and F. S. SPRING (Rec. trav. chim., 1938, 57, 529–534).— BzO_2H and Δ^4 -cholestene in CHCl_3 give a homogeneous *oxide* (I), m.p. 100–101°, $[\alpha]_D^{19}$ +81.7°, which with a little H_2SO_4 in AcOH gives *5-hydroxy-4-acetoxycholestane* (II), m.p. 175°, $[\alpha]_D^{20}$ +184°, hydrolysed by 10% $\text{KOH}-\text{EtOH}$ to the (OH)₂-compound, m.p. 169–170°. (II) is resinified by dehydrating agents and converted into (I) by $\text{K}-\text{CS}_2-\text{MeI}$ in C_6H_6 ; (IV) (below) is similarly converted into $\alpha-\Delta^5$ -cholestene oxide (III). 5 : 6-Dihydroxycholestane with Ac_2O gives the 6-*acetate* (IV), m.p. 108–109°. Hydrogenation (colloidal Pd) of (I) and (III) gives cholestane. $\text{EtOH}-\text{conc. HCl}$ dehydrates (I), (II), (III), and (IV) to the cholestadiene, m.p. 80–81°, $[\alpha]_D^{25}$ -68.5° (absorption max. at 2350 and 2450 Å. in EtOH). Cholesteryl chloride gives similarly an *oxide*, m.p. 97.5°, $[\alpha]_D^{25}$ -34.95°, and 3-chloro-5-hydroxy-6-acetoxycholestane, m.p. 147–147.5°, $[\alpha]_D^{19}$ -17.5°. Hydrogenation (PtO_2) of 7-keto- $\Delta^{3,5}$ -cholestadiene in EtOAc gives 7-keto- (V) and 7-hydroxy-cholestane, m.p. 119–120°, $[\alpha]_D^{19}$ +50.6° [better obtained from (V) by $\text{Na}-\text{C}_5\text{H}_{11}\cdot\text{OH}$; oxidised to (V) by CrO_3 ; *H phthalate*, m.p. 165–167°].

R. S. C.

$\Delta^{5,7}$ -Androstadiene-3 : 17-diol. A. BUTEN-ANDT, E. HAUSMANN, and J. PALAND [with, in part, D. VON DRESLER and U. MEINERTS] (Ber., 1938, 71, [B], 1316–1322).— Δ^5 -Androstenediol diacetate

is oxidised by CrO_3 in AcOH at 55° to 7-keto- Δ^5 -androstene-3 : 17-diol diacetate (I), m.p. 218–219°, $[\alpha]_D^{20}$ -135° in CHCl_3 , hydrolysed (NaOMe) to 7-keto- Δ^5 -androstene-3 : 17-diol (+ H_2O), m.p. 201°, $[\alpha]_D^{20}$ -133° in EtOH . Boiling $\text{MeOH}-\text{HCl}$ converts (I) into $\Delta^{5,7}$ -androstadiene-17-ol-7-one, m.p. 171–172°, $[\alpha]_D^{20}$ -375° in EtOH (*acetate*, m.p. 222°, $[\alpha]_D^{20}$ -400° in CHCl_3). With $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH (I) yields Δ^5 -androstene-3 : 7 : 17-triol, m.p. 236°, $[\alpha]_D^{23}$ +26° in EtOH [*tribenzoate* (II), m.p. 250°, $[\alpha]_D^{23}$ +87° in CHCl_3]. Slow distillation of (II) in a high vac. or, better, treatment of it with boiling NPhMe_2 affords $\Delta^{5,7}$ -androstadiene-3 : 17-diol dibenzoate, m.p. 217–218°, hydrolysed to $\Delta^{5,7}$ -androstadiene-3 : 17-diol (III), m.p. 212° (*diacetate*, m.p. 132°, $[\alpha]_D^{23}$ +41° in EtOH). The absorption spectrum of (III) is almost identical with that of ergosterol and 7-dehydrocholesterol, thus supporting the assigned constitution. The physiological properties of the compounds are detailed. H. W.



(III.)

Sterols. XXXIV. Isolation of hexahydro- α -estradiols from human non-pregnancy urine. R. E. MARKER, E. ROHRMANN, E. L. WITTLE, and E. J. LAWSON (J. Amer. Chem. Soc., 1938, 60, 1512–1513; cf. A., 1938, II, 329).—Female non-pregnancy urine contains *hexahydro- α -estradiols*, (I), m.p. 242° (*diacetate*, m.p. 160°), and (II), m.p. 204° (*diacetate*, m.p. 160°), both indifferent to Br and digitonin and converted by Pt-black into equilenin. (II) is identical with a diol obtained from *cestrone* by Dirscherl (A., 1936, 472) and gives a *diketone*, $\text{C}_{18}\text{H}_{26}\text{O}_2$, m.p. 148°; (I) gives an isomeric *diketone*, m.p. 124°. (I) and (II) differ in configuration at $\text{C}_{(6)}$ or $\text{C}_{(10)}$. They are not present in pregnancy urine. R. S. C.

Biological formation of *epi*etiocholanediol.—See A., 1938, III, 660.

Preparation of polyhydroxypregnane compounds. A. SERINI and W. LOGEMANN (Ber., 1938, 71, [B], 1362–1366).—17-Ethynylisoandrostanediol is hydrogenated ($\text{Ni}-\text{MeOH}$) to 17-vinyl-isoandrostanediol (I), m.p. 207°, which is converted by permonophthalic acid in CHCl_3 into the corresponding *oxide*, m.p. 180–182°, and by OsO_4 followed by Na_2SO_3 in boiling $\text{EtOH}-\text{H}_2\text{O}$ into 3 : 17 : 20 : 21-tetrahydroxy-allopregnane, m.p. 230–232°. Addition of Br in CCl_4 to (I) in $\text{Et}_2\text{O}-\text{CCl}_4$ containing a little $\text{C}_5\text{H}_5\text{N}$ affords 5 : 6-dibromo-17-vinylandrostanediol, m.p. 116–118° (decomp.), transformed by OsO_4 followed by Na_2SO_3 and then by Zn dust into 3 : 17 : 20 : 21-tetrahydroxy- $\Delta^{5,6}$ -pregnene, m.p. 229–231°, $[\alpha]_D^{20}$ -73.3° in dioxan, whence (Ac_2O in anhyd. $\text{C}_5\text{H}_5\text{N}$ at room temp.) the 3 : 20 : 21-triacetate, m.p. 166–167°, $[\alpha]_D^{20}$ -88.5° in dioxan. 17 : 20 : 21-Trihydroxy- $\Delta^{4,6}$ -pregnen-3-one, m.p. 233–235°, $[\alpha]_D^{20}$ +65.6° in dioxan [*semicarbazone*, m.p. 216–218° (decomp.)], is obtained by the successive action of OsO_4 and Na_2SO_3 on pregnadiene-17-ol-3-one, and is converted by $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ at room temp. into the 20 : 21- Ac_2 derivative, m.p. 178–179°, $[\alpha]_D^{20}$ +43.6° in dioxan. H. W.

Alkyl and alkamine esters of *p*-aminomandelic acid and related compounds. L. S. FOSDICK

and G. D. WESSINGER (J. Amer. Chem. Soc., 1938, 60, 1465—1466).— p -NO₂·C₆H₄·CH(OH)·CN with the appropriate alcohol and HCl in Et₂O at 0° gives the imino-ether hydrochloride, hydrolysed by H₂O to Me, m.p. 87°, Et, m.p. 76—77°, Prⁿ, m.p. 84—84.5°, Buⁿ, m.p. 44—45°, and β -chloroethyl p -nitromandelate, m.p. 79.5—80°, hydrogenated (PtO₂) in EtOH to Me, m.p. 162°, Et, m.p. 119—119.5°, Prⁿ, m.p. 84—84.5°, Buⁿ, m.p. 104—105°, and β -chloroethyl (I) p -aminomandelate, m.p. 95—96°. With NHR₂ at 100° (I) gives β -di-ethyl- (II) [hydrochloride, m.p. 129—133° (decomp.)], -propyl- [hydrochloride, m.p. 135—140° (decomp.)], and -butyl-aminoethyl p -aminomandelate [hydrochloride, m.p. 150—155° (decomp.)]. (II) is a rather weak local anæsthetic. M.p. are corr.

R. S. C.

Hydrogenation of compounds containing halogen using platinum-black. G. VAVON and R. MATHIEU (Compt. rend., 1938, 206, 1387—1389).—Many Cl- and Br-compounds in EtOH are easily reduced by H₂-Pt-black. The latter react the more readily, particularly if halogen is linked to a C adjacent to Ph or CO₂H. $\alpha\beta$ -Dibromo- β -phenylpropionic acid, its Et ester and amide, $\alpha\beta$ -dibromo- β -phenylethyl Me ketone, $\alpha\beta$ -dibromo- α -phenylpropane, and CHMeBr·CHBr·CO₂H first absorb 2 H to give 2 HBr and the corresponding ethylenes, which are then further reduced. Similar Cl₂-compounds react more slowly; intermediates could not be isolated.

J. L. D.

Constituents of natural phenolic resins. X. Structure of *l*-matairesinol dimethyl ether: condensation of reactive methylene groups with *O*-methyleugenol oxide. R. D. HAWORTH and J. R. ATKINSON (J.C.S., 1938, 797—808; cf. A., 1936, 985).—*l*-Matairesinol Me₂ ether (I) with dil. NaOH at 180°, boiling 50% KOH, or EtOH-NaOEt followed by boiling dil. HCl yields a mixture, $[\alpha]_D^{17}$ about +18° in CHCl₃, of (I) with *d*-isomatairesinol Me₂ ether, m.p. 111—112°, $[\alpha]_D^{19}$ +78° in CHCl₃ [Br₂, m.p. 144°, $[\alpha]_D^{20}$ +18.8° in CHCl₃, and (NO₂)₂-derivative, m.p. 161—162°, $[\alpha]_D^{20}$ +105.5° in CHCl₃]. Cold MeOH-KOH converts this into (I), and hot NaOH into the equilibrium mixture, $[\alpha]_D$ +18°. It is hydrolysed [MeOH-Ba(OH)₂] at the same rate as (I), and with Pb(OAc)₄ gives the cyclodehydrolactones also obtained (*loc. cit.*) from (I). The Na salt from (I) and MeOH-NaOMe with dil. AcOH gives the *OH*-acid, m.p. 90—95° (loss of H₂O), resolidifying with m.p. 127°, $[\alpha]_D^{18}$ —32° in EtOH. When the mixed acids from (I) and NaOH at 180°, pptd. by AcOH, are boiled with EtOH, the *l*-acid is preferentially lactonised, leaving (after extraction with CHCl₃) the *d*-isohydroxy-acid, m.p. 160°, $[\alpha]_D^{18}$ —23° in EtOH. It is concluded that the *l*- and *d*-isolactones are *trans*- and *cis*-, respectively. The synthetic isomeride (II) (*loc. cit.*) with Pb(OAc)₄ gives a mixture of two diacetates, C₂₆H₃₀O₉, m.p. 150—151°, and C₂₆H₃₀O₁₀, m.p. 158—159°, hydrolysed to compounds, C₂₂H₂₆O₈, m.p. 101—103°, and C₂₂H₂₄O₇, m.p. 147—148°, respectively, both oxidised (KMnO₄) to veratric acid. β -Veratroyl-*n*-butyric acid when reduced (Na + EtOH) and lactonised (dil. acid) yields γ -(3:4-dimethoxyphenyl)- β -methyl- γ -butyrolactone, m.p. 112—113°, differing from (II). CH₂Ph·CN, Et succinate, and NaOEt

yield 2-cyano-2-phenylcyclopentane-1:3-dione, m.p. 149°, hydrolysis of which presented difficulties. 3:4-(OMe)₂C₆H₃·CH₂·COCl with CH₂N₂ followed by Et₂O-HCl affords veratryl CH₂Cl ketone, m.p. 52°, which could not be condensed with CH₂(CO₂Et)₂, whilst 3:4-CH₂O₂·C₆H₃·CH₂·COCl treated similarly gives 2-chloropiperonyl CH₂Cl ketone (?), m.p. 107—108°, one Cl of which is hydrolysed by MeOH-KOH.

3:4-(OMe)₂C₆H₃·CH₂·COCl with Et sodioacetosuccinate, followed by hydrolysis, yields γ -keto- γ -veratrylbutyric acid (an oil), reduced (Na + EtOH) and lactonised to γ -veratryl- γ -butyrolactone, m.p. 83—84° (NO₂-derivative, m.p. 115—116°), also prepared from *O*-methyleugenol oxide and CHNa(CO₂Et)₂, or by hydrolysing its α -Ac derivative (*loc. cit.*). It differs from (II), is oxidised (KMnO₄) to veratric acid, and is not cyclised by MeOH-HCl, AcOH-HCl, or 80% H₂SO₄. Piperonyl chloride and Et sodioacetoglutarate yield an acid which when reduced and lactonised gives γ -(3:4-methylenedioxybenzyl)- γ -butyrolactone, b.p. 170—180°/0.1 mm. (NO₂-derivative, m.p. 98—99°). Na α -acetyl- γ -(3:4-methylenedioxybenzyl)- γ -butyrolactone and 3:4-methylenedioxybenzyl chloride yield an α -Ac-derivative, b.p. 270—280°/1 mm., hydrolysed to $\alpha\gamma$ -bis-(3:4-methylenedioxybenzyl)butyrolactone, identical with that obtained (*loc. cit.*) from safrole oxide. From the above it appears that active CH₂ groups react with the γ -C of *O*-methyleugenol and safrole oxides, and that (II) is $\alpha\gamma$ -diveratryl- γ -butyrolactone. On this basis a list of corr. formulæ is given. (II) is hydrolysed [as for (I)] to γ -hydroxy- $\alpha\gamma$ -bis-(3:4-dimethoxybenzyl)butyric acid, an oil. α -Acetyl- γ -veratryl- γ -butyrolactone is hydrolysed to the hydroxyketone, b.p. 185—188°/0.3 mm.; with conc. HCl-AcOH this gives 6:7-dimethoxy-3:1-endomethyleneoxy-1-methyl-1:2:3:4-tetrahydronaphthalene, m.p. 96°, whilst the lactone itself gives the -2-carboxylic acid, m.p. 182—183° (Me ester, m.p. 142°). Either product with Se at 280° yields 6:7-dimethoxy-1:3-dimethylnaphthalene, m.p. 97—98° (picrate, m.p. 119—120°), also synthesised by reducing (Clemmensen) β -veratroyl-*n*-butyric acid, heating the product with 80% H₂SO₄, and treating the resulting 1-keto-6:7-dimethoxy-3-methyl-1:2:3:4-tetrahydronaphthalene, m.p. 132—133°, with MgMeI, followed by Se. Similarly Me γ -hydroxy- γ -piperonylpropyl ketone and α -acetyl- γ -(3:4-methylenedioxybenzyl)- γ -butyrolactone yield 6:7-methylenedioxy-3:1-endomethyleneoxy-1-methyl-1:2:3:4-tetrahydronaphthalene, m.p. 85—86°, and the -2-carboxylic acid, m.p. 219—220° (Me ester, m.p. 156—157°), respectively. It is suggested that a pinacolinic transformation occurs in the formation of these naphthalene derivatives.

O-Benzylvanillin with CN·CHNa·CO₂Na in EtOH-NaOH, followed by HCl, yields α -cyano- β -(*O*-benzylvanillyl)acrylic acid, m.p. 202°, reduced (Na-Hg) and esterified (MeOH-HCl) to Me α -cyano- β -(*O*-benzylvanillyl)propionate, m.p. 72°. CH₂Ph·CO·CH₂·OPh is reduced [Al(OPrⁱ)₃ + PrⁱOH] to β -hydroxy- γ -phenoxy- α -phenylpropane, m.p. 92°. 3:4-(OMe)₂C₆H₃·CH₂·CN, OPh·CH₂·CO₂Me, and NaOEt yield α -cyano- β -keto- γ -phenoxy- α -(3:4-dimethoxyphenyl)propane, m.p. 111—112°, hydrolysed by fuming HCl-AcOH in the cold to β -keto- γ -phenoxy-

α -(3:4-dimethoxyphenyl)butyramide, m.p. 173°, which when boiled with 8% HCl gives γ -phenoxy- α -(3:4-dimethoxyphenyl)acetone, m.p. 63–64°, reduced [Al(OPrⁱ)₃] to the sec.-alcohol, m.p. 100°. Veratrole and glutaric anhydride with AlCl₃ in PhNO₂ yield γ -veratroyl-, m.p. 140–142°, reduced (Clemmensen) to γ -veratryl-*n*-butyric acid, m.p. 78°. A. Li.

Two stereoisomeric 2-methylcyclohexanol-1-carboxylic acids. M. GODCHOT and (Mlle.) G. CAUQUIL (Compt. rend., 1938, 206, 1523–1525; cf. A., 1937, II, 63, 149).—The NaHSO₃ compound of 2-methylcyclohexanone (I) with KCN affords a cyanohydrin which with conc. HCl affords about 20% of a mixture of 2-methylcyclohexanol-1-carboxylic acids [separated by fractional crystallisation into a form, m.p. 109° (II) (*Me* ester, b.p. 99°/15 mm.; *anilide*, m.p. 129°; *NH*₄ salt), and a little of an *isomeride*, m.p. 70–71° (*Me* ester, b.p. 89–90°/15 mm.; *anilide*, m.p. 84°; *NH*₄ salt)], and neutral substances which with boiling 30% KOH afford (I) and (II). J. L. D.

Resolution of 3:3'-dibromo- and 3:3'-disulpho-*cyclobutanespirocyclobutane-3:3'-dicarboxylic acids*. H. J. BACKER and H. G. KEMPER (Rec. trav. chim., 1938, 57, 761–769).—Addition of Br to CO₂H-CH<CH₂>C<CH₂>CH-CO₂H and red P and then heating first at 100° and finally at 130–140°, gives 79% of 3:3'-dibromocyclobutanespirocyclobutane-3:3'-dicarboxylic acid (I), m.p. 182–183° (decomp. at about 230°) (*dichloride*, b.p. 163–164°/5 mm., m.p. 37.5–38.5°; *Me*₂, b.p. 153–154°/2.5 mm., *Et*₂, b.p. 160°/2.5 mm., *Bu*₂, m.p. 80–81°, and *Ph*₂ ester, m.p. 90.5–91.5°; *diamide*, m.p. 175.5–176°; *dianilide*, m.p. 187.5–188.5°), resolved by brucine to the *d*-acid, [*M*]_D +5.4° in EtOH (Na₂ salt, [*M*]_D +14.4° in H₂O). (I) is hydrolysed by shaking in H₂O with Ag₂CO₃ to the 3:3'-(OH)₂-acid (*Ba*, +H₂O, and *diquinine* salt, +2H₂O), and converted (as *NH*₄ salt) by (NH₄)₂SO₃ at 75° into the 3:3'-disulpho-3:3'-dicarboxylic acid [*tetraquinine*, +9H₂O, *tetrastrychnine*, +9H₂O, *Ba*₂, +5H₂O (3H₂O lost at 150°/vac.), and *TL*₄ salt], which is resolved by way of the polybrucine salt to the *d*-acid (Na₄ salt, [*M*]_D +26.6°). R. S. C.

Influence of directing groups on nuclear reactivity in oriented aromatic substitutions. III. Nitration of ethyl benzoate. C. K. INGOLD and M. S. SMITH (J.C.S., 1938, 905–917; cf. A., 1928, 164; 1931, 1405).—Nitration of an equimol. mixture (large excess) of C₆H₅ and EtOBz with AcNO₃ in Ac₂O at 18° for 6 hr. shows that C₆H₅ is nitrated 272 ± 6 times as rapidly as EtOBz. The products are extracted with Et₂O, treated with Na₂SO₃ and NaHCO₃ to remove C(NO₂)₄, and hydrolysed, the PhNO₂ separated from the mixed NO₂-acids by Et₂O extraction in NaOH solution, and both determined by reduction with excess of TiCl₃. Nitration of EtOBz under the same conditions produces the *o*-, *m*-, and *p*-NO₂-isomerides in the ratio 24:72:4. The acids obtained by alkaline hydrolysis are extracted with Et₂O, BzOH removed by steam distillation, and each acid is determined by extracting the solid mixture with H₂O saturated with the other two, and measuring the increased acidity, correction being made for

alterations in solubility, and for traces of BzOH. These results indicate partial rate factors: *o*-, 0.0026, *m*-, 0.0079, and *p*-, 0.0009. A. Li.

β -Monoalkylaminoethyl *p*-aminobenzoates.—See B., 1938, 847.

Isomorphism of organic compounds. IV. H. LETTRÉ and H. BARNBECK (Ber., 1938, 71, [B], 1225–1228; cf. A., 1938, II, 139).—Examination of a series of substituted benz-*p*-nitroanilides shows that here as in the case of substituted benzoic acids H is not isomorphously replaceable by Cl, Br, or Me. The mixed crystal formation of Bz derivatives substituted in the same position by Cl, Br, or Me corresponds with that of the benzoic acids themselves. Structural isomerides are incapable of forming mixed crystals. The following benz-*p*-nitroanilides appear new: *o*-, *m*-, and *p*-chloro-, m.p. 187, 197°, and 221°, respectively; *o*-, *m*-, and *p*-bromo-, m.p. 199°, 194°, and 247°, respectively; *o*-, *m*-, and *p*-methyl-, m.p. 177.5°, 151°, and 206.5°, respectively. H. W.

Stereochemistry of diphenyls. XLIII. Effect of substituents in the 4-position of 2-nitro-2'-methoxydiphenyl-6-carboxylic acid. R. ADAMS and H. R. SNYDER. XLIV. *Meso*- and racemic isophthalamides of 3-nitro-3'-aminodimesityl. R. ADAMS and R. M. JOYCE, jun. (J. Amer. Chem. Soc., 1938, 60, 1411–1415, 1489–1491; cf. A., 1936, 723).—XLIII. The rate of racemisation of 2-nitro-2'-methoxydiphenyl-6-carboxylic acid is very little affected by NO₂, Cl, Br, or Me in position 4, in contrast to the great effect of these substituents in position 3', 4', or 5'. The effect of a substituent thus depends on the nature of the other groups in the ring substituted. 5-Bromoisatoic anhydride, m.p. 286–288° (decomp.), prepared from 5-bromoisatin and CrO₃-AcOH at 10–15°, is converted by NaNO₃-H₂SO₄ at 5–10° into 5-bromo-7-nitroisatoic anhydride (I), m.p. 94°, and 5-bromo-3-nitro-2-aminobenzoic acid (II), m.p. 245–247° [obtained from (I) by hot HCl-AcOH]. With K₂S₂O₅-fuming HNO₃, followed by I-KI, (II) yields 5-bromo-2-iodo-3-nitrobenzoic acid, m.p. 213–214.5°, the *Me* ester, m.p. 63°, of which with *o*-C₆H₄I-OMe and activated Cu-bronze at 210–230° gives a product, hydrolysed to dl-4-bromo-2-nitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. 181°, resolved by strychnine into the *l*-acid, [α] –46° in EtOH (all rotations are at 28° for the *D* line) [*strychnine* salt, m.p. 139° (decomp.), [α] –166° in CHCl₃]. Similarly are prepared 5-chloro-, m.p. 267° (decomp.), and 5-chloro-7-nitro-isatoic anhydride, m.p. 85°, 5-chloro-3-nitro-2-amino-, m.p. 240°, and 5-chloro-2-iodo-3-nitro-benzoic acid, m.p. 204° (*Me* ester, m.p. 66–67°), dl-, m.p. 171°, and 1-4-chloro-2-nitro-2'-methoxydiphenyl-6-carboxylic acid, [α] –24.5° in EtOH [*strychnine* salt, m.p. 137° (decomp.), [α] –120° in CHCl₃]. 7-Nitro-5-methylisatoic anhydride (modified prep.), new m.p. 177°, and boiling dil. HCl yield 5-nitro-4-amino-*m*-toluic acid, m.p. 256–257° (decomp.); the position of the NO₂ in these compounds is proved by conversion by diazotisation (Cu-bronze) into 5:1:3-NO₂-C₆H₃Me-CO₂H, new m.p. 175.5–176.5°: 4-Iodo-5-nitro-*m*-toluic acid, m.p. 207–209° (*Me* ester, m.p. 43–44°), dl-, m.p. 179°, and 1-2-nitro-2'-methoxy-4-methylidiphenyl-6-carboxylic acid, m.p. 175–178°,

$[\alpha] -30^\circ$ in EtOH [strychnine salt, m.p. 143° (decomp.), $[\alpha]$ about -110° in CHCl_3], are prepared. 3 : 2 : 1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{H}$ and fuming $\text{HNO}_3\text{--H}_2\text{SO}_4$ give 3 : 5 : 2 : 1- $(\text{NO}_2)_2\text{C}_6\text{H}_2\text{Br}\cdot\text{CO}_2\text{H}$, new m.p. $215\text{--}216^\circ$, and thence by way of the Me ester thereof, m.p. $106\text{--}108^\circ$, dl., m.p. 185° , and 1 : 2 : 4-dinitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. $182\text{--}185^\circ$, $[\alpha] -12^\circ$ in EtOH [strychnine salt, m.p. 136° (decomp.), $[\alpha]$ about -185° in CHCl_3].

XLIV. 3 : 3'-Dinitrodimesityl (modified prep.), m.p. $162\text{--}163^\circ$ (corr.), and anhyd. $\text{SnCl}_2\text{--HCl--AcOH}$ give 3-nitro-3'-aminodimesityl (III), m.p. $145\text{--}146^\circ$ [hydrochloride, m.p. $244\text{--}247^\circ$ (decomp.) (sinters at 236°)], which with $m\text{-C}_6\text{H}_4(\text{COCl})_2$ and $\text{C}_5\text{H}_5\text{N}$ in C_6H_6 give isophthaldi-3 : 3'-nitromesitylmesitylamide, (?) meso-, m.p. 302° , and (?) dl-form, m.p. 247° (corr.). $\text{COCl}\cdot[\text{CH}_2]_4\cdot\text{COCl}$ and (III) give only one form of adipdi-3 : 3'-nitromesitylmesitylamide, m.p. $230\text{--}231^\circ$ (corr.). $(\text{COCl})_2$, however, gives fractions, m.p. $304\text{--}307^\circ$ (corr.) and $273\text{--}283^\circ$ (corr.), which could not be obtained pure. CS_2 and (III) in KOH--EtOH give 3-nitrodimesityl-3'-thiocarbimide, m.p. $119\text{--}120^\circ$.

R. S. C.

Synthesis of 5-chloro-10-methyl-1 : 2-benzanthracene and related compounds. M. S. NEWMAN (J. Amer. Chem. Soc., 1938, 60, 1368—1370).—The Grignard reagent from $o\text{-C}_6\text{H}_4\text{ClBr}$ with 1 : 2- $\text{C}_{10}\text{H}_6(\text{CO})_2\text{O}$ in $\text{Et}_2\text{O--C}_6\text{H}_6$ gives 43% of 2-*o*-chlorobenzoyl-1-naphthoic acid, m.p. $202\text{--}202.8^\circ$, the structure of which is proved by decarboxylation to $\text{C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Cl}\cdot o$, identified as 2 : 4-dinitrophenylhydrazones, m.p. $265.2\text{--}266.2^\circ$. With MgMeBr the acid gives 79% of the lactone, m.p. $122\text{--}122.6^\circ$, of 2- α -hydroxy- α -*o*-chlorophenylethyl-1-naphthoic acid, reduced (Zn dust, aq. NaOH) to 2- α -*o*-chlorophenylethyl-1-naphthoic acid, m.p. $168\text{--}168.8^\circ$. With H_2SO_4 this gives 5-chloro-10-methyl-1 : 2-benzanthracene, m.p. $133\text{--}133.4^\circ$ (purified by way of the picrate, m.p. $141.8\text{--}142.4^\circ$; oxidation gives only a trace of a substance, m.p. $175\text{--}176^\circ$; a by-product, m.p. $133\text{--}133.4^\circ$, is also formed), converted by CuCN in $\text{C}_5\text{H}_5\text{N}$ at 260° into 5-cyano-10-methyl-1 : 2-benzanthracene, m.p. $182.8\text{--}183.2^\circ$, and thence by 65% H_2SO_4 in AcOH into 10-methyl-1 : 2-benzanthracene-5-carboxylamide, m.p. $308\text{--}310^\circ$ (uncorr.). M.p. are corr.

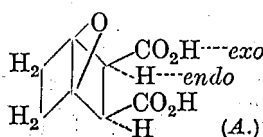
R. S. C.

Condensations by sodium. XII. Mechanism of formation of phenylmalonic acid and the syntheses of butyl- and phenyl-malonic acids from monocarboxylic acids. A. A. MORTON, F. FALLWELL, jun., and L. PALMER (J. Amer. Chem. Soc., 1938, 60, 1426—1429; cf. A., 1937, II, 101).—When $\text{CHPh}(\text{CO}_2\text{Na})_2$ is prepared from $\text{C}_6\text{H}_{11}\text{Cl}$, Na, and C_6H_6 by successive addition of PhMe and CO_2 , reaction proceeds by way of NaPh, NaCH_2Ph , $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$, and $\text{CHPhNa}\cdot\text{CO}_2\text{Na}$. The presence of NaPh is proved by adding CO_2 before the PhMe and thus forming BzOH. That of NaCH_2Ph is proved by adding MeI or BuCl instead of CO_2 , thus forming PhEt or $\text{PhC}_5\text{H}_{11}$, respectively. That of $\text{CHPhNa}\cdot\text{CO}_2\text{Na}$ is proved by the fact that more $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ is formed at the expense of $\text{CHPh}(\text{CO}_2\text{Na})_2$ if the CO_2 is added more rapidly, and by the prep. of $\text{CHPh}(\text{CO}_2\text{Na})_2$ from isolated $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ by $\text{NaPh--CO}_2\text{Na}$ hexoate and NaPh

in boiling C_6H_6 lead to $\text{CHBu}^+(\text{CO}_2\text{Na})_2$; with $\text{NaC}_5\text{H}_{11}$ in light petroleum at 45° no reaction occurs. Addition of MeI to NaPh and PhMe at room temp. gives PhEt, indicating presence of NaCH_2Ph in the mixture, but CO_2 gives only BzOH; when NaPh and PhMe are heated at 60° for 2 hr., CO_2 then leads to much $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$, but formation of NaCH_2Ph is complete (as judged by the acids formed) only at 75° . Only traces of $\text{C}_6\text{H}_4(\text{CO}_2\text{Na})_2$ are formed. R. S. C.

Electrolysis of aromatic acids. VII. [Potassium] alkyl phthalates. V. M. RODIONOV and V. C. ZVORIKINA (Bull. Soc. chim., 1938, [v], 5, 840—847; cf. A., 1937, II, 291).—Electrolysis (Pt anode, Hg cathode) of K Et phthalate (I) yields 50—55% of Et H $\Delta^{2:6}$ -dihydrophthalate (II), m.p. $121\text{--}122^\circ$, hydrolysed to *trans*- $\Delta^{2:6}$ -dihydrophthalic acid, m.p. $222\text{--}223^\circ$ (cf. von Baeyer, A., 1892, 1211) [the anhydride (III), m.p. $84\text{--}85^\circ$, is convertible by EtOH into (II)], phthalide (29%), and small amounts of EtOBz and hydrodiphthalyls. K Me phthalate similarly yields phthalide, PhCHO, and Me H $\Delta^{2:6}$ -dihydrophthalate, m.p. $125\text{--}126^\circ$, also obtained from (III) and MeOH. Electrolysis of (I) with a diaphragm gives phthalide, phthalic and dihydrophthalic acids, but no (II). Electrolysis (Pt electrodes) of (I) yields only a little EtOBz, suggesting that K—Hg is the reagent which forms (II). Electrolysis (Hg cathode) of α - and β -Et K hemipinates affords mainly unchanged material, with a little ψ -meconine and meconine, respectively. A. T. P.

Steric course of additive and substitutive reactions. IX. Steric course of the catalytic hydrogenation of double linkings in dicyclic systems. *endo*- and *exo*-Isomerism. K. ALDER and K. H. BAEKENDORF (Annalen, 1938, 535, 113—122).—Reduction of the double linking in the 3 : 6-*endo*-oxido-system follows the reverse course to that in the *dicyclo*-[1 : 2 : 2]-heptene system. Whereas in the latter the H addition proceeds from the CH_2 bridge, in the former under the same conditions the same addendum does not proceed from the O bridge but from the *endo*-position of the double linking. 3 : 6-*endo*-Oxido- Δ^1 -tetrahydrophthalic acid is hydrogenated (PtO₂ in AcOH) to *exocis*-3 : 6-*endo*oxido-



hexahydrophthalic acid (cf. A), m.p. $169\text{--}170^\circ$, converted by boiling AcCl into the corresponding anhydride, m.p. $158\text{--}159^\circ$; it is converted by CH_2N_2 into the Me₂ ester, from which *trans*-3 : 6-*endo*-oxido-hexahydrophthalic acid is obtained by alkaline hydrolysis. Hydrogenation of 3 : 6-*endo*oxido-3-methyl- Δ^1 -tetrahydrophthalic acid leads to *exocis*-3 : 6-*endo*oxido-3-methylhexahydrophthalic acid, m.p. $160\text{--}161^\circ$ (anhydride, m.p. $87\text{--}89^\circ$). Similarly, 3 : 6-*endo*oxido-3 : 6-dimethyl- Δ^1 -tetrahydrophthalic acid yields *exocis*-3 : 6-*endo*oxido-3 : 6-dimethylhexahydrophthalic acid, m.p. $202\text{--}203^\circ$ (anhydride, m.p. $175\text{--}177^\circ$), the Me₂ ester, m.p. $41\text{--}42^\circ$, of which is hydrolysed by alkali to the corresponding *trans*-acid. H. W.

New cholesterol derivatives. A. DANSI (Gazzetta, 1938, 68, 273—276).— $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgCl}$ and β -cholestanone (I) in Et_2O yield, after distillation and

dehydration by KHSO_4 , 3- β -phenyl-ethylcholestene (or -ethylidenecholestane), m.p. 94–95°, $[\alpha]_D^{20} +61^\circ$ in CCl_4 . Similarly, cholestenone (II) gives 3- β -phenyl-ethylcholestadiene (or -ethylidenecholestene), m.p. 94–95°, $[\alpha]_D^{20} -131^\circ$ in CCl_4 . With Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in C_6H_6 , (I) yields, after hydrolysis, 3-carboxymethylcholestene (or 3-carboxymethylenecholestane), m.p. 161°, $[\alpha]_D^{20} +60^\circ$ in CCl_4 , and (II) gives 3-carboxymethylcholestadiene (or 3-carboxymethylenecholestene), m.p. 221–223°, $[\alpha]_D^{20} +199^\circ$. E. W. W.

Bile acids. LIV. M. SCHENCK (Z. physiol. Chem., 1938, 253, 244–252; cf. A., 1938, II, 99).—The β -acid $\text{C}_{24}\text{H}_{34}\text{O}_{10}\text{N}_2$ (I) boiled for 20 min. with 10% HCl gives the NH_2 -acid B, $\text{C}_{24}\text{H}_{36}\text{O}_{11}\text{N}_2$ (II), decomp. 155–160°, also obtained (with decomp. $\sim 167^\circ$) from the isomeric NH_2 -acid A (III) (from the α -acid by cleavage of the lactam ring) and 90% H_2SO_4 at 100° for 15 min. With alkaline KMnO_4 (I) loses approx. 33% of its N in gaseous form; similarly (II) [but not (III)] also yields a gas (probably N_2). Formulae taking account of these results are proposed for the acids. W. McC.

Attempted syntheses of the antirachitic vitamin. I. Syntheses of β -unsaturated alcohols and aldehydes with hemicyclic double linking. K. DIMROTH [in part with JONSSON] (Ber., 1938, 71, [B], 1333–1345).—Attempts are described to obtain simple systems containing three hemicyclic double linkings arranged as in vitamin- D_2 . cyclo-Hexylideneacetic acid is converted through the chloride into cyclohexylideneacet-o-toluidide, m.p. 105–106°; under mild conditions this reacts with PCl_5 in C_6H_6 at 0° or with SOCl_2 alone or in CCl_4 or C_6H_6 giving cyclohexenylacet-o-toluidide, m.p. 126°, identical with the synthetic material. 1-Ethynylcyclohexanol is hydrogenated (Pd sponge) to 1-vinylcyclohexanol (I), which is slowly converted by Ac_2O at 100° into cyclohexylidene-ethyl alcohol (II), b.p. 95–96°/13.5 mm. (dinitrobenzoate, m.p. 90–91°), accompanied by much vinylcyclohexene. (II) is preferably obtained by the use of $\text{CCl}_3\text{CO}_2\text{H}\cdot\text{Ac}_2\text{O}\cdot\text{AcOH}$ at 55°; at $>55^\circ$ or if reaction is prolonged, the yellow, condensed hydrocarbons are obtained. PBr_3 and $\text{C}_2\text{H}_5\text{N}$ transform (I) into cyclohexylidene-ethyl bromide, b.p. 80–81°/12 mm., transformed by KOAc followed by hydrolysis into (II). Addition of $\text{CrO}_3\cdot\text{AcOH}$ to (II)- $\text{C}_6\text{H}_5\cdot\text{AcOH}$ affords cyclohexylideneacetaldehyde, b.p. (indef.) 86–92°/13.5 mm. [additive compound with NaHSO_3 ; semicarbazone, m.p. about 210° (decomp.), according to the manner of heating], characterised by oxidation to cyclohexylideneacetic acid, m.p. 91°. For comparison cyclohexenylethyl alcohol is oxidised to cyclohexenylacetaldehyde (semicarbazone, m.p. 177°). trans-2-Ketodecahydronaphthalene, $\text{C}_{20}\text{H}_{18}$, and K amyloxyde yield trans-ethinyldecahydro- β -naphthol, b.p. 122–128°/13 mm., m.p. 91.5°, reduced (Pd in MeOH) to trans-vinyldecahydro- β -naphthol, m.p. 72°, which is isomerised to trans-2-decahydronaphthylidenylethyl alcohol (p-nitrobenzoate, m.p. 99°), oxidised to trans-2-decahydronaphthylidenylacetaldehyde [additive compound with NaHSO_3 ; semicarbazone, m.p. 229–230° (decomp.)]. trans-Ethinyldecahydro- α -naphthol, b.p. 120–121°/12 mm. (p-nitrobenzoate,

m.p. 111°), is reduced to trans-vinyldecahydro- α -naphthol, b.p. 116–121°/11 mm. This is isomerised to 1-decahydronaphthylidenylethyl alcohol, b.p. 151–152°/12 mm. (dinitrobenzoate, m.p. 99°, with apparently an isomorphous form which softens at 75°), whence 1-decahydronaphthylidenylacetaldehyde [semicarbazone, m.p. 235° (decomp.)], oxidised to 1-decahydronaphthylidenylacetic acid, m.p. 155–156°. H. W.

Induced oxidation of iodobenzene during the oxidation of benzaldehyde.—See A., 1938, I, 406.

Velocity of the Cannizzaro reaction.—See A., 1938, I, 404.

Thioketonic esters. VI. S. K. MITRA (J. Indian Chem. Soc., 1938, 15, 129–132).—The reaction between RCHO and β -thioketonic esters to give β -trithioaldehydes (I) probably occurs by hydrolysis of an intermediate, additive hydroxy-sulphide to $\text{OH}\cdot\text{CHR}\cdot\text{SH}$, which loses H_2O to give (I). Et methylthioacetoacetate with PhCHO , anisaldehyde, vanillin, and CH_2O in $\text{EtOH}\cdot\text{HCl}$ gives respectively β -trithiobenzaldehyde, β -trithioanisaldehyde, β -trithiovanillin, and β -trithioformaldehyde (II), m.p. 218°. Et sodiothioacetoacetate in C_6H_6 with $\text{CH}_2\text{Cl}\cdot\text{OME}$ affords Et β -methoxymethylthiol- α -methylcrotonate, b.p. 120°/12 mm., which with aq. HBr gives (II). A. L.

Reaction of magnesium phenyl bromide with β -methoxy- β -mesitylacrylonitriles. R. C. FUSON, G. E. ULLYOT, R. F. STEDMAN, and P. O. TAWNEY (J. Amer. Chem. Soc., 1938, 60, 1447–1450).—Either form of 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{C(OMe)}\cdot\text{CH}\cdot\text{CN}$ (I) or the 1:1 mol. compound of the two reacts with MgPhBr (usually 5 mols.) to give amounts, which vary according to the conditions used, of α -imino- γ -methoxy- α -phenyl- γ -mesityl- Δ^{β} -propene hydrobromide (II), m.p. varies between 110° and 130°, β -imino- β -phenylpropio-mesitylene (III), m.p. 145.5–146.5°, γ -methoxy- α -phenyl- γ -mesityl- Δ^{β} -propen- α -one (IV), m.p. 111.5–112.5°, and $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COPh}$ (V); some of the lower-melting form of (I) is always recovered, isomerisation taking place under the conditions of reaction. Melting of (II) is accompanied by decomp. to (III) and MeBr . NaNH_2 and Me_2SO_4 convert (V) into (IV). $\text{NH}_3\cdot\text{MeOH}$ converts (V) into (III), but yields NH_2Bz and COPhMe or COPhEt , respectively, from CH_2Bz_2 or CHMeBz_2 . Hydrolysis of (II), (III), or (IV) by aq. $\text{EtOH}\cdot\text{HCl}$ gives (V). 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{C(OMe)}\cdot\text{CMe}\cdot\text{CN}$ and MgPhBr give similarly α -imino- γ -methoxy- α -phenyl- γ -mesityl- β -methyl- Δ^{β} -propene hydrobromide (VI), m.p. 110–130° (decomp.), and α -phenyl- γ -mesityl- β -methylpropane- $\alpha\gamma$ -dione (VII), an oil (Cu derivative) [obtained also by hydrolysis of (VI)]. At the m.p. (VI) gives MeBr and an oil, which is probably α -imino- α -phenyl- γ -mesityl- β -methylpropan- γ -one, since hydrolysis gives (VII). (VII) has been synthesised from $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{COEt}$. Methylquinolinium bromide has m.p. 96–97° (lit. 70°). R. S. C.

Double reductions. Z. C. GLACET and J. WIEMANN (Compt. rend., 1938, 206, 1736–1737).—Reduction (Zn dust) of a mixture of PhCHO and Ac_2 under the conditions described by Wiemann (cf. A., 1936, 589) affords β -acetyl- α -phenylpropylene glycol (unstable), isolated as its CMe_2 ether, b.p. 70°/about

10 mm. $\text{CH}_2\text{:CH}\cdot\text{CHO}$ and Ac_2 similarly afford $\gamma\delta$ -dihydroxy- δ -acetyl- Δ^a -pentene (CMe_2 ether, b.p. 81—82°/14 mm.). J. L. D.

Reactivity of nitrosyl chloride. R. PERROT (Compt. rend., 1938, 206, 1575—1577; cf. A., 1934, 1216).—Deoxybenzoin with NOCl at 80° rapidly (slowly at room temp.) affords $\text{COPh}\cdot\text{CHPhCl}$. Benzilmonoxime is formed at room temp. in the absence of light. MeCN with NOCl at 200° affords a little AcCl . $\text{CHCl}_2\cdot\text{CN}$ behaves similarly but also gives $\text{CCl}_2\cdot\text{CN}$, which at >220° affords C_2Cl_6 and $(\text{CN})_2$. HCN at 200° similarly affords CNCl which is somewhat polymerised. At 350°, CO and NOCl afford COCl_2 . CPh:CPh with NOCl at 150—200° affords BzCl .

J. L. D.

Attempted synthesis of the antirachitic vitamin. II. Condensation of cyclohexylideneacetaldehyde with cyclohexanone. K. DIMROTH (Ber., 1938, 71, [B], 1346—1350).—cycloHexanone is condensed with cyclohexylideneacetaldehyde by 1% aq. NaOH under N_2 at room temp. to α -cyclohexylidene- β -2-ketocyclohexylidene-ethane (I), m.p. 67°. This when treated with MgMeI and then distilled in a vac. gives an oil which is very sensitive to air. (I) is treated with Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in C_6H_6 and the product is hydrolysed and distilled, thus yielding α -cyclohexylidene- β -2-methylenecyclohexylidene-ethane, the absorption spectrum of which resembles that of tachysterol much more closely than that of vitamin- D_2 . H. W.

Diphenylketazine oxide. K. VON AUWERS (Ber., 1938, 71, [B], 1260).—The spectrochemical behaviour of the compound obtained by oxidising $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$ with $\text{K}_3\text{Fe}(\text{CN})_6$ harmonises with the formula $\text{CPh}_2\cdot\text{NO}\cdot\text{N}\cdot\text{CPh}_2$ and not $\text{CPh}_2\cdot\text{N}\cdot\text{N}\cdot\text{CPh}_2$ proposed by Schönberg *et al.* (A., 1938, II, 298). H. W.

Diaryl ketone peroxides. C. S. MARVEL and V. E. NICHOLS (J. Amer. Chem. Soc., 1938, 60, 1455—1457).—Passing O_3 into $\text{CPh}_2\cdot\text{CHR}$ ($\text{R} = \text{H}$, Me , or Et), but not $\text{CPh}_2\cdot\text{C}\cdot\text{CHBu}^v$, in CCl_4 under varied conditions gives some BzOH and 3—7% of dimeric benzophenone peroxide (I), m.p. 206.5—207.5° to 214.5—215.5° (decomp.). The dimerides, m.p. 210.5—211.5° (decomp.), 183—184° (decomp.), and 186.5—187.5° (decomp.), of *di*-*p*- and *m*-tolyl and *Ph p*-tolyl ketone peroxide, respectively, were similarly obtained in 3—7% yield with some of the acids formed by cleavage of the ketone. $\text{CH}_2\text{:C}(\text{C}_6\text{H}_4\text{Ph})_2$ gives no ketone peroxide, but yields *p*-carboxyphenyl diphenyl ketone, m.p. 287—288°. The dimerides sublime slightly at the m.p., and decompose partly when recrystallised, but are unusually inert to reagents. $\text{Zn}\cdot\text{AcOH}$ reduces (I) to $\text{COPh}\cdot\text{CPh}_3$; $\text{Al}\cdot\text{Hg}$ gives $\text{CHPh}_2\cdot\text{OH}$; at 214—215° (I) gives COPh_2 . (I) is obtained in 3% yield by keeping CPh_2Cl_2 in 30% H_2O_2 for 2 weeks, but not from COPh_2 by H_2O_2 , $\text{H}_2\text{O}_2\text{--H}_2\text{SO}_4$, $\text{H}_2\text{S}_2\text{O}_8$, or O_3 . as-*Di*-*m*-tolylethylene, b.p. 134—139°/5 mm., is prepared by adding EtOAc to *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ and heating the carbinol at 210—215°. *Di*-*m*-tolyl ketone has m.p. 51°. R. S. C.

Deformations of valency angles according to absorption spectra; structures of benzo-

cyclanones, their oximes, and benzocyclenes. (MME.) P. RAMART and J. HOCH (Bull. Soc. chim., 1938, [v], 5, 848—871).—Partly a more detailed account of work previously reviewed (A., 1936, 471). Much of the following appears new (cf. A., 1935, 621). The absorption spectra of $\text{C}_6\text{H}_4\cdot\text{C}(\text{CH}_2)_n\text{CH}$ ($\text{R} = \text{H}$ and Me , $n = 1, 2$) and $\text{C}_6\text{H}_4\cdot\text{C}(\text{C}(\text{CH}_2)_n\text{CMe}_2)\text{CMe}_2$ ($n = 1, 2$) are compared; the latter are also compared with the oximes of $\text{C}_6\text{H}_4\cdot\text{C}(\text{CH}_2)_n\text{CR}_2$ ($\text{R} = \text{H}$ and Me). COPhPr^{β} (+ NaNH_2) and $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{Br}$ give *Ph* γ -phenyl- α -dimethylpropyl ketone, b.p. 206—208°/15 mm., converted by NaNH_2 in PhMe into the amide, m.p. 108°, of γ -phenyl- α -dimethylbutyric acid, m.p. 98°, b.p. 176—180°/13 mm., the chloride, b.p. 137—139°/18 mm., of which with AlCl_3 in light petroleum below 30° for 24 hr. yields 1-keto-2:2-dimethyl-1:2:3:4-tetrahydronaphthalene, b.p. 147°/25 mm. (oxime, m.p. 131°). Similarly *Ph* δ -phenyl- α -dimethylbutyl ketone, b.p. 219—220°/20 mm., yields the amide, m.p. 91°, of δ -phenyl- α -dimethylvaleric acid, m.p. 35°, b.p. 180—181°/10 mm., the chloride of which is cyclised to (probably) 2-phenyl-5:5-dimethylcyclopentanone.

2:2-Dimethylbenzsuberone, $\text{C}_6\text{H}_4\cdot\text{C}(\text{CH}_2)_3\text{CMe}_2$, b.p. 140°/16 mm. (oxime, m.p. 139°), is prepared from benzsuberone (2-oximino-derivative, m.p. 136°) and $\text{MeI}\cdot\text{NaNH}_2$ (cf. Haller and Bauer, A., 1910, i, 490). 2:2-Dimethyl-1-ethylidene-indane, b.p. 112—114°/13 mm., and 1:2:3:4-tetrahydronaphthalene, b.p. 122—123°/14 mm., are prepared by dehydration ($\text{AcCl}\cdot\text{Ac}_2\text{O}$) of $\text{C}_6\text{H}_4\cdot\text{C}(\text{CH}_2)_n\text{CMe}_2$ (from the ketone and MgEtBr). *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CMe}_2\cdot\text{OH}$ could not be dehydrated. *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COEt}$ and $\text{MeCHO}\cdot\text{HCl}$ (saturated) give *o*-tolyl α -methyl- Δ^a -propenyl ketone, b.p. 127°/10 mm.; 1-keto-2-ethylidene-1:2:3:4-tetrahydronaphthalene, m.p. 45—46°, b.p. 158—160°/10 mm., is similarly prepared. A. T. P.

Keto-enol tautomerism of acenaphthenone. (SIGNA.) E. GHIGI (Gazzetta, 1938, 68, 184—192).—Acenaphthenone (I) in aq. $\text{EtOH}\cdot\text{KOH}$ with PhN_2Cl or *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ gives the mono-phenyl- or *o*-anisyl-hydrazone (cf. A., 1916, i, 212) of acenaphthenequinone (II), by isomerisation of the corresponding azo-derivative of enolic (I). Similarly (I) in aq. $\text{EtOH}\cdot\text{KOH}$ with NaNO_2 , rapidly acidified by HCl , yields the monoxime of (II). Attempts to isolate the enol of (I) by Hieber's method (A., 1921, ii, 466) were unsuccessful. $\text{K}_3\text{Fe}(\text{CN})_6$ and (I) in $\text{EtOH}\cdot\text{KOH}$ give 7:7'-diacenaphthyliden-8-one (III) (A., 1896, i, 444), whilst FeCl_3 gives 7:7'-diacenaphthenonyl (A., 1938, II, 20). With boiling Ac_2O , (I) yields 8-acetoxy-7-acetylacenaphthylene (?) (IV), m.p. 133—134°, hydrolysed (H_2SO_4) to a substance (V), m.p. 117°, or (NaOH) to (III) with traces of (V). It is suggested that (IV) is formed by way of acetoxiacenaphthylene and acetylacenaphthenone, by repeated enolisation.

E. W. W.

Syntheses in the naphthindene series. G. WOJACK, S. GLUPE, and H. JATZKEWITZ (Ber., 1938,

71, [B], 1372—1381).—Et α -1-naphthoylpropionate is converted by the successive action of PCl_5 in CCl_4 and AcCl containing a little conc. H_2SO_4 into 3-chloro-2-methyl-4:5-benzoindone (I), m.p. 133° , transformed by warm conc. H_2SO_4 or by NaOH - EtOH into 2-methyl-4:5-benzoindane-1:3-dione, m.p. 110° . Et α -2-naphthoylpropionate (II) is converted by PCl_5 first in boiling CCl_4 and subsequently at 140° into 2:3:3-trichloro-2-methyl-6:7-benzoindane-1-one (III), m.p. 95° , whence (conc. H_2SO_4 at 70 – 80°) 2-chloro-2-methyl-4:5-benzoindanedione, m.p. 132° . Partial dehalogenation of (III) by Cu powder in abs. EtOH at about 90° gives 3-chloro-2-methyl-6:7-benzoindone, m.p. 97° , also obtained from (II) and PCl_5 (1:1) in CCl_4 and then accompanied by β -chloro- β -2-naphthyl- α -methylacrylic acid, m.p. 145° . Successive additions of SO_2Cl_2 and PCl_5 to Et 2-naphthylacetate (IV) in CCl_4 and final heating of the mixture at 150° leads to 2:2:3:3-tetrachloro-6:7-benzoindane-1-one (V), m.p. 135° , transformed by 96% H_2SO_4 at 110 – 120° into 2:2-dichloro-6:7-benzoindane-1:3-dione, m.p. 182° , which is converted by HI (d 1.7) and red P into 6:7-benzoindane-1:3-dione, m.p. 177 – 178° (decomp.). Cu powder in boiling EtOH transforms (V) into 2:3-dichloro-6:7-benzoindone, m.p. 136° . (IV) and PCl_5 (3.5 mols.) in CCl_4 give mainly β -chloro-, m.p. 214° (decomp.), and $\alpha\beta$ -dichloro- β -2-naphthylacrylic acids, m.p. 172° . 1-Naphthylacrylic acid is converted into the dibromide, m.p. 189° (decomp.), transformed by anhyd. KOH in boiling EtOH into 1-naphthylpropionic acid, m.p. 137° . This is transformed by boiling AcOH - Ac_2O into 8- α -naphthylphenanthrene-6:7-dicarboxylic anhydride, m.p. 206° , and by the successive action of Br in Et_2O and P_2O_5 at 85° into 2:3-dibromo-4:5-benzoindone, m.p. 168° [oxidised by HNO_3 at 140° to 1:2:3:4- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$]. H. W.

Attempted preparation of ninhydrin from 2-nitroindane-1:3-dione. G. WANAG and A. LODE (Ber., 1938, 71, [B], 1267—1272).—The decomp. of 2-nitroindane-1:3-dione (I) by heat gives indication of the formation of ninhydrin (II) (bisphenylhydrazone, new m.p. 180°) which could not thus be obtained cryst. Decomp. in a vac. is sometimes accompanied by violent explosion. In boiling AcOH (I) yields hydrindantin, m.p. 236° (red at 200°) (also + $2\text{H}_2\text{O}$) (cf., Ruhemann, J.C.S., 1911, 99, 792), and an amorphous yellow compound, m.p. about 135° (decomp.). Oxidation of (I) gives o - $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ as the only isolable product. 2-Bromo-2-nitroindane-1:3-dione does not give appreciable amounts of (I) when heated by itself, whereas in boiling PhNO_2 (II) is obtained in about 40% yield accompanied by 2:2-dibromoindanedione, m.p. 178° . Rapid passage of Cl_2 through a solution of (I) in H_2O gives 2-chloro-2-nitroindane-1:3-dione (III), m.p. 124° , decomp. about 150° , in 89.1% yield; the yield diminishes if the passage of Cl_2 is prolonged on account of the oxidation to o - $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$. In boiling PhNO_2 (III) affords (II) (yield 22.5—45%) and dichloroindanedione, m.p. 124° . H. W.

Steroids and sex hormones. XLIV. Elimination of hydrogen bromide from 2-bromocholestanone and 2-bromoandrostanedione. L. RUZICKA, P. A. PLATTNER, and R. AESCHBACHER

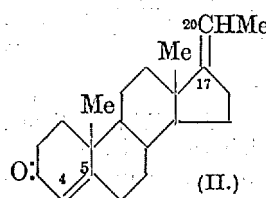
(Helv. Chim. Acta, 1938, 21, 866—872).—2-Bromocholestanone is converted by boiling $\text{C}_6\text{H}_5\text{N}$ into 3-keto-2-cholestanolpyridinium bromide, m.p. 310° (decomp.) when placed in a preheated bath, which in EtOH gives an immediate ppt. of AgBr when treated with AgNO_3 . It passes when distilled at 250 – 300° /10 mm. into Δ^4 -cholestenone, m.p. 80 – 80.5° , $[\alpha]_D^{25} +87^\circ$ in EtOH. Analogously, 3:17-diketo-2-androstanylpyridinium bromide (+ H_2O), m.p. about 315° (decomp.), affords Δ^4 -androstene-3:17-dione, m.p. 172 – 173° , $[\alpha]_D^{25} +193^\circ$ in CHCl_3 . That Br is at $\text{C}_{(2)}$ is proved by conversion of 2-bromocholestan-3-one by NaOAc in boiling AcOH into 2-acetoxycholestan-3-one, m.p. 146° , which is hydrolysed to 2-hydroxycholestan-3-one, m.p. 126° ; this is oxidised to the dicarboxylic acid, $\text{C}_{27}\text{H}_{46}\text{O}_4$, m.p. 196° , identical with that derived directly from cholestanol. H. W.

Transformation products of 17-ethyltestosterone. A. BUTENANDT, J. SCHMIDT-THOMÉ, and H. PAUL (Ber., 1938, 71, [B], 1313—1316; cf. A., 1936, 727).—An improved method for the conversion of dehydroandrosterone into 17-ethyltestosterone (I) is described. Dehydration of

(I) is best effected by distillation with anhyd. CuSO_4 in a high vac. and the product is identified as Δ^4 -5-17:20-pregnadien-3-one (II), m.p. 135° , since it is converted by successive treatment with OsO_4 in Et_2O and aq. EtOH - Na_2SO_3 into Δ^4 -pregnene-17:20-diol-3-one, m.p. 199° , which is oxidised by $\text{Pb}(\text{OAc})_4$ to MeCHO and the known Δ^4 -androstene-3:17-dione.

Colouring matter of the lobster (*Astacus gammarus*, L.). R. KUHN and N. A. SÖRENSEN (Angew. Chem., 1938, 51, 465—466; cf. A., 1933, 509).—"Ovoverdin" from fresh lobster eggs is purified by repeated adsorption on $\text{Al}(\text{OH})_3$, extraction with 40% $(\text{NH}_4)_2\text{SO}_4$, and pptn. with 65% $(\text{NH}_4)_2\text{SO}_4$. Fission of "ovoverdin" (dil. acids, EtOH, COMe_2 , or heat) yields astaxanthin (I), $\text{C}_{40}\text{H}_{52}\text{O}_4$, a di- α -ketol [and not an ester (cf. loc. cit.)], which is autoxidised by alkali to astacin, and gives blue salts with alkali in absence of O_2 . (I) is formulated as a diketodihydroxy- β -carotene, and the blue colour of the "ovoverdin" is ascribed to salt formation between (I) and proteins. J. D. R.

Formation of isomeric phenylhydrazones in the Japp-Klingemann reaction. A. SEMPRONJ (Gazzetta, 1938, 68, 263—271).—2- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Cl}$ with NaOEt and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ gives Et α -acetyl- β -2-naphthylpropionate, b.p. 180° /1.2 mm.; which in EtOH with aq. NaOH and PhN_2Cl yields, after hydrolysis, 2-naphthylpyruvic acid phenylhydrazone (I), m.p. 187 – 188° , with β -2-naphthylpropionic acid, m.p. 134 – 135° . With EtOH- HCl , (I) forms 3- β -naphthylindole-2-carboxylic acid, m.p. 223 – 224° (decomp. to 3- β -naphthylindole, m.p. 141 – 142°). 2- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CN}$ and $\text{Et}_2\text{C}_2\text{O}_4$ with NaOEt furnish the Na derivative of Et β -cyano- β -2-naphthylpyruvate, m.p. 143 – 144° , hydrolysed to β - $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, giving the normal phenylhydrazone. 1:2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{CH}_2\text{Br}$ with NaOEt and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ gives



Et α -acetyl- β -1-bromo-2-naphthylpropionate, which in EtOH with NaOH and PhN_2Cl gives, after hydrolysis, two stereoisomeric 1-bromo-2-naphthylpyruvic acid phenylhydrazones, m.p. 178° and 187–188°; both of these give, after hydrolysis, 3-(1'-bromo-2'-naphthyl)indole-2-carboxylic acid, m.p. 240° (decomp.). 1:2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{CH}_2\cdot\text{CN}$ with $\text{Et}_2\text{C}_2\text{O}_4$ and NaOEt yields the Na derivative of Et β -cyano- β -1-bromo-2-naphthylpyruvate, m.p. 194–195°, hydrolysed (H_2SO_4) to 1-bromo-2-naphthylpyruvic acid, m.p. 190–191°, which gives the phenylhydrazone of m.p. 187–188° (see above). E. W. W.

Degradation of deoxycholic acid to α tiodeoxycholic acid through α tiodeoxycholy methyl ketone. W. M. HOEHN and H. L. MASON (J. Amer. Chem. Soc., 1938, 60, 1493–1497).—Deoxycholic acid is degraded by the Barbier-Wieland process (cf. A., 1927, 247) to α tiodeoxycholic acid (I), m.p. 283–286°, $[\alpha]_{\text{D}}^{25} +102 \pm 1.5^\circ$. Oxidation of the diphenyl-carbinols or -ethylenes by CrO_3 in hot AcOH gives about 50% yields, but at $<15^\circ$ gives 70% yields. In the last stage direct oxidation of α -diphenyl- β -3:12-diacetoxynorcholanyl ethylene, m.p. 215–217°, $[\alpha]_{\text{D}}^{25} +537^\circ$ in EtOH, gives only 16% of (I), but ozonolysis (excess of O_3 to be avoided) in CHCl_3 to 3:12-diacetoxyltiocolanyl Me ketone (II), m.p. 121–122.5°, $[\alpha]_{\text{D}}^{25} +190.4 \pm 2.5^\circ$ in EtOH, condensation with PhCHO by NaOEt (which partly hydrolyses the OAc), reacetylation by Ac_2O , ozonisation of the crude product to the glyoxal (not purified), oxidation thereof by HIO_4 in aq. EtOH, and finally hydrolysis by hot 2N-NaOH give an over-all yield of about 40% of (I). The following intermediates are described. α -Diphenyl- β -3:12-diacetoxynorcholanyl ethylene, m.p. 160°, $[\alpha]_{\text{D}}^{25} +118 \pm 2^\circ$ in EtOH; nordeoxycholic acid, + COMe_2 , double m.p. 140–145° and 206–210°, $[\alpha]_{\text{D}}^{25} +62 \pm 2.5^\circ$ in EtOH; α -diphenyl- β -3:12-diacetoxyltiocolanyl ethylene, m.p. 158–160°, $[\alpha]_{\text{D}}^{25} +183 \pm 2^\circ$ in EtOH; bisnordeoxycholic acid, + H_2O , double m.p. 195–202° and 236–238°, $[\alpha]_{\text{D}}^{25} +35.8 \pm 5^\circ$ in EtOH. 2N-KOH hydrolyses (II) to 3:12-dihydroxytiocolanyl Me ketone, m.p. 165–166°, $[\alpha]_{\text{D}}^{25} +165 \pm 5^\circ$ in EtOH, converted by CrO_3 into 3:12:17-triketotiocolane, m.p. 189–191°, $[\alpha]_{\text{D}}^{25} +235 \pm 2.5^\circ$ in EtOH. Dehydro-nor-, m.p. 230–232°, $[\alpha]_{\text{D}}^{25} +114 \pm 2^\circ$ in EtOH, -bisor-, m.p. 275–276° (sinters at 265°), $[\alpha]_{\text{D}}^{25} +98 \pm 5^\circ$ in EtOH, and - α tiodeoxycholic acid, m.p. 177–178.5°, $[\alpha]_{\text{D}}^{25} +166 \pm 4^\circ$ in EtOH, are prepared. M.p. are corr. R. S. C.

Sterols. XXXIII. 3:11-Dihydroxy-12-ketocholanic acid and derivatives [thereof]. R. E. MARKER and E. J. LAWSON (J. Amer. Chem. Soc., 1938, 60, 1334–1337; cf. A., 1938, II, 276).—Partial hydrogenation of dehydrodeoxycholic acid gives a mixture (not a mol. compound) of 3-(α -) (I) and 3-(β -)hydroxy-12-ketocholanic acid (cf. Kyogoku, A., 1937, II, 150). When deoxycholic acid is heated with slightly >0.5 mol. of Ac_2O in AcOH at 135° and then oxidised with CrO_3 in 50% AcOH at 20–30°, the product after hydrolysis may be separated into deoxycholic acid and (I), anhyd., m.p. 161–162°, and + C_6H_6 , double m.p. 110° and 161–162° (Ac derivative, m.p. 195°). Ruzicka and Goldberg's

prep. (A., 1935, 749) of lithocholic acid, m.p. 184°, from (I) is improved. The semicarbazone of (I) has m.p. 241°. With 3Br_2 at 60–80° the Ac derivative of (I) gives a Br_2 -derivative, but when treated with $\text{Br}\cdot\text{HBr}$ in $\text{Ac}_2\text{O}\cdot\text{AcOH}$ at 70° and then hydrolysed by KOH-aq. MeOH, gives 3(α):11-dihydroxy-12-ketocholanic acid, m.p. 196° (3-Ac derivative, m.p. 268°; semicarbazone, m.p. 238°); this resists Clemmensen reduction owing to steric protection of the CO by the OH; the 11-OH is readily removed by dehydration. R. S. C.

New degradation of digoxigenin. M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 828–844).—Identical products, as expected from the present constitutional formulæ of digoxigenin (I) and corticosterone (II), are not obtained by the oxidation of these substances. It is therefore probable that OH placed at present at C_{11} in (I) and (II) has actually a different position. Digoxigenin diacetate is oxidised by KMnO_4 in COMe_2 at room temp. to 14-hydroxy-3:(?)11-diacetoxyltiocolanic acid, m.p. 229–230°, hydrolysed (KOH-MeOH) to 3:(?)11:14-trihydroxytiocolanic acid (III), different samples m.p. 246–247° (decomp.), 214–215° (decomp.), and 188–190° (probably minute amounts of impurities have a very pronounced effect on the m.p.) (Me ester, m.p. 90–95° and 208–212° after re-solidification at about 125°). This is oxidised by CrO_3 in AcOH at room temp. to 14-hydroxy-3:(?)11-diketotiocolanic acid, m.p. 236–237° (Me ester, m.p. 174–178°). 5% H_2SO_4 converts (III) in dioxan at 100° into a mixture of acids including cryst. 3:(?)11-dihydroxytiocolanic acid (IV), m.p. 282–286° (decomp.) (hygroscopic Me ester, m.p. 170–172°); this is hydrogenated with extreme difficulty and is oxidised (CrO_3 in AcOH at room temp.) to a substance, m.p. 220–235°. The amorphous material obtained from the mother-liquors of (IV) is esterified (CH_2N_2), hydrogenated (PtO_2), and hydrolysed to 3:(?)11-dihydroxytiocolanic acid, m.p. 280–286° (slight decomp.), the Me ester, m.p. 180–183°, of which is oxidised to Me 3:(?)11-diketotiocolanate (V), m.p. 171–172°, $[\alpha]_{\text{D}}^{25} +138.3^\circ \pm 2^\circ$ in MeOH. 3:(?)11-Diketotiocolanic acid is reduced (Zn-Hg and conc. HCl) to α tiocolanic acid. (V) is transformed by the successive action of $\text{Br}\cdot\text{HBr}\cdot\text{AcOH}$ and boiling $\text{C}_6\text{H}_5\text{N}$ into Me Δ^4 -3:(?)11-diketotiocolanate, m.p. 236–237°, $[\alpha]_{\text{D}}^{25} +185^\circ \pm 2^\circ$ in MeOH, to which the corresponding ester derived from (II) could not be isomerised. All m.p. are corr. H. W.

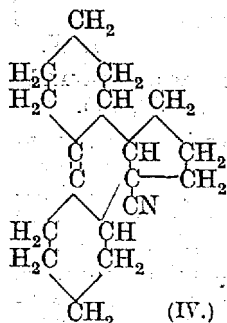
Conversion of leuco-anthraquinone compounds into their oxidised forms.—See B., 1938, 765.

Action of ammonia on anthraquinone in presence of reducing agents. K. LAUER, T. AOYAMA, and H. SHINGU (Ber., 1938, 71, [B], 1151–1157).—Anthraquinone (I) is converted by $\text{Na}_2\text{S}_2\text{O}_4$ (3 mols.) and NH_3 (d 0.88) at 150° into anthraquinol (II), anthranol (III), dianthranol (IV), 9-aminoanthracene (V) (main product), and the very unstable, yellow 9-imino-9'-keto-10:10'-dihydrodianthryl (VI), m.p. 265–266° (decomp.). This is sol. in warm alkali, cannot be methylated or acetylated, does not give a vat, and does not couple. The Ac derivative, m.p. 272–273°, of (V) with Me_2SO_4 and EtOH-alkali gives a Me deriv-

ative, m.p. 195—200° (decomp.). (IV) and (VI) arise from secondary oxidations. (II) is transformed by NH_3 under pressure and in the absence of a reducing agent into (V) (yield about 25%) whilst about 50% of (II) is recovered [as (I)]; (VI) and 9:9'-*di-imino*-10:10'-*dihydrodianthrlyl*, m.p. 204—205°, but not (III), are also formed in small proportion. Increase in the amount of $\text{Na}_2\text{S}_2\text{O}_4$ causes diminution in the total yield and in that of (V), reduction proceeding extensively to the anthracene stage before reaction with NH_3 occurs. Under similar conditions halogeno- or sulpho-anthraquinones give the corresponding amines without loss of the usually mobile substituent. The behaviour of Na_2SO_3 resembles that of $\text{Na}_2\text{S}_2\text{O}_4$.

H. W.

Synthesis of polycyclic compounds from di-cyclohexenyl. C. WEIZMANN, E. BERGMANN, and T. BERLIN (J. Amer. Chem. Soc., 1938, 60, 1331—1334).—The adduct, m.p. 113—115°, of di- Δ^1 -cyclohexenyl (I) and $(\text{CH}\cdot\text{CO})_2\text{O}$ is dehydrogenated by S at 245° to phenanthrene-9:10-dicarboxylic anhydride (II), m.p. 312°, but by $\text{Pb}(\text{OAc})_4$ only to the 1:2:3:4:5:6:7:8- H_8 -anhydride, m.p. 305°. With MgPhBr (II) gives 9-benzoylphenanthrene-10-carboxylic acid, m.p. 218°, and thence $(\text{P}_2\text{O}_5$ on chloride in decahydronaphthalene) 1:2:3:4-dibenzanthraquinone (III), m.p. 180°. *o*-9-Phenanthroylbenzoic acid [prep. from $\text{C}_{14}\text{H}_9\cdot\text{MgBr}$ and *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ with, in some cases, *di*-9-phenanthrylphthalide, m.p. 239°, as a by-product] gives the impure chloride, m.p. 165—166° (decomp.), which is converted (as above) into (III). $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ and (I) at 180° give 9-phenyl- $\Delta^{12:13}$ -*dodecahydronaphthalene*-10-carboxylic acid, m.p. 221°; $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ gives the corresponding *Et* ester, m.p. 85—86°, which is resistant to hydrolysis; the acid with Se at 300—320° gives 9-phenylphenanthrene, m.p. 113°, but with S at 260° yields 9-phenylphenanthrene-10-carboxylic acid. With $p\text{-O}\cdot\text{C}_6\text{H}_4\cdot\text{O}$ at 140° (I) gives the normal adduct, *eicositetrahydrotetrazabenzanthraquinone*, m.p. 247°, together with $p\text{-C}_6\text{H}_4(\text{OH})_2$ and (?) *s*-tetra(tetramethylene)-1:4:5:8-tetrahydroanthraquinone, m.p. 297°. The product, m.p. 315° (decomp.), described by Barnett and Lawrence (A., 1935, 1243) was not obtained. The normal adduct is not obtained from (I) and α -naphthaquinone, but, instead, the partly dehydrogenated deca-, m.p. 254°, and octa-hydro-1:2:3:4-dibenzanthraquinone, m.p. 238—239°, and 1:4- $\text{C}_{10}\text{H}_6(\text{OH})_2$ are formed. 1-Cyano- Δ^1 -cyclopentene and (I) at 150—160° give only a trace of the adduct (IV), b.p. 210—220°/1.5 mm. Mg 9-phenanthryl bromide and $\text{CH}(\text{OEt})_3$ give phenanthrene-9-aldehyde *Et*₂ acetal, b.p. 175°/0.75 mm., hydrolysed to the free aldehyde, m.p. -98°, b.p. 200°/1.5 mm., which leads to β -9-phenanthryl-acrylic, m.p. 255°, and -propionic acid, m.p. 178°, cyclised by P_2O_5 in PhMe at 100° to 4:5:6:7-dibenzhydrindone, m.p. 164°; Clemmensen reduction then yields 9:10-cyclopentenophenanthrene, m.p. 164°. With phenyl-*p*-benzoquinone at 120—125° (I) gives 2-phenyl-5:6:7:8-bistetramethylene-5:8:9:10-



(IV.)

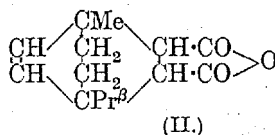
tetrahydronaphtha-1:4-quinone, m.p. 207—208°, but in PhNO_2 dehydrogenation to 2-phenyl-5:6:7:8-bistetramethylene-5:8-dihydronaphtha-1:4-quinone, m.p. 140—141°, occurs simultaneously. 2:3-Dimethylindone and (I) in PhMe at 200° give 9:10-dimethyl-*s*-dodecahydronaphthalene-9:10-2:3-hydrindone, b.p. 165—175°/0.1 mm., reduced (Clemmensen) to the corresponding hydrindene derivative, b.p. 240—245°/0.1 mm., dehydrogenation of which at 300° gives traces of a substance, m.p. >300°, and an oil (picrate, m.p. 210°).

R. S. C.

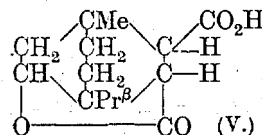
Chenopodium oil. III. Ascaridole. H. PAGET (J.C.S., 1938, 829—833).—Ascaridole (I) has m.p. 2°, b.p. 113—114°/20 mm., $[\alpha]_D -0.03^\circ$; repeated crystallisation has not indicated any separation. Reduction (TiCl_3) gives C_3H_8 and *p*-cresol, together with very small amounts of an unsaturated glycol, $\text{C}_{10}\text{H}_{18}\text{O}_2$, m.p. 84°, a chlorotrihydroxymenthane (?), m.p. 191° (mono-*p*-nitrobenzoate, m.p. 124°), and ascaridole ω -glycol (mono-, m.p. 150°, and di-*p*-nitrobenzoate, m.p. 174°). Hydrogenation (Pd) of (I) affords *cis*-1:4-terpin (mono-, m.p. 117°, and di-*p*-nitrobenzoate, m.p. 172°), whilst with $\text{PtO}_2\text{-H}_2$ dihydroascaridole, m.p. 19.5°, $[\alpha]_D \pm 0^\circ$, is obtained. This is reduced (TiCl_3) to 1-methylcyclohexan-1-ol 3:4-oxide (?), m.p. 45° (mono-*p*-nitrobenzoate, m.p. 157°), and C_3H_8 . Partial hydrogenation (Pd-C) of (I) yields Δ^2 -*p*-menthene-1:4-diol (di-*p*-nitrobenzoate, m.p. 130°).

F. R. S.

Diene synthesis. XXIX. α -Terpinene. O. DIELS, W. KOCH, and H. FROST (Ber., 1938, 71, [B], 1163—1172).— α -Terpinene (I) and maleic anhydride give *cis*-3-methyl-6-isopropylendoethylenetetrahydrophthalic anhydride (II), b.p. 195°/12 mm., m.p. 66—67° [corresponding acid (III), m.p. 158° (decomp.), and its Na salt]. (II) is converted by $\text{MeOH-H}_2\text{SO}_4$



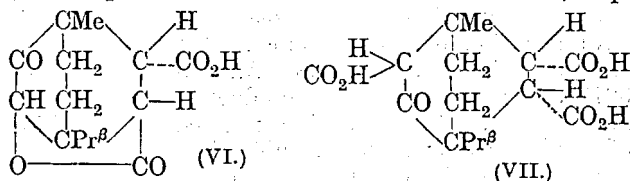
(II.)



(V.)

into the Me_2 ester, b.p. 175—180°/15 mm., hydrolysed by NaOH-MeOH to *trans*-3-methyl-6-isopropylendoethylenetetrahydrophthalic acid (IV), m.p. 203°. Hydrogenation (colloidal Pd-MeOH) followed by distillation of (III) gives *cis*-3-methyl-6-isopropylendoethylenehexahydrophthalic anhydride, m.p. 54°, identical with the product obtained directly from (II). Similarly (IV) is reduced to *trans*-3-methyl-6-isopropylendoethylenehexahydrophthalic acid, m.p. 218°. There is therefore no need to doubt the structure already assigned to (I). Lactonisation of (II) or (III) proceeds with exceptional difficulty (50% H_2SO_4 at 100° for 6 days for a partial change) and is accompanied by a *trans*-isomerisation of the free CO_2H , the product therefore being the *lactonic acid* (V), m.p. 169—170°. The *cis*-lactonic acid, m.p. 185°, is obtained by debromination of the monobromolactonic acid (VI), m.p. 178° (slight decomp.), obtained by the action of $\text{Br-H}_2\text{O}$ on (III); it is isomerised to (V) by treatment with CH_3N_3 followed by alkaline hydrolysis. $\text{KOH-MeOH-H}_2\text{O}$ followed by Ac_2O transform (VI) into the dilactone, $\text{C}_{14}\text{H}_{18}\text{O}_4$, m.p. 235°. Oxidation of (II) with

KMnO₄ gives in small amount a *ketocislactonic acid* (VI), m.p. 218°, characterised as the *Me* ester, m.p.



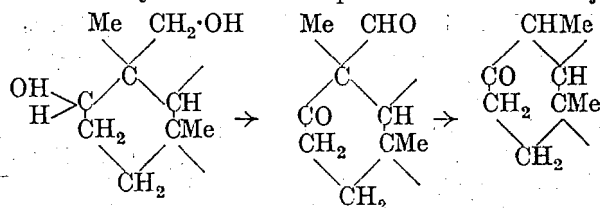
161°, whilst a second oxidation product is a *hydroxy-ketodicarboxylic acid* (VII), m.p. 216° (decomp.) (*Me*₂ ester, m.p. 150°; *anhydride*, m.p. 198°). No evidence of the formation of the expected (CO₂H)₄ acid was obtained. Ozonisation of (II) in EtOAc and treatment of the product with H₂-Pd-CaCO₃ affords a neutral compound, m.p. 214°, which cannot be esterified and does not give the customary reactions for ketones. Δ³-Carene (VIII) differs from (I) in containing a 3-membered ring in place of a double linking so that the conjugation in (I) is replaced by that of a double linking and a 3-membered ring; this is frequently ruptured during additive reactions and behaves as a double linking. If this is here the case (II) must also result from (VIII) and maleic anhydride. Actually a well-defined adduct is obtained, converted by NaOH into an acid, C₁₄H₂₀O₄, m.p. 184° (decomp.) (*Na* salt), which is not identical with (III) and of which the structure is not established. H. W.

Anomalous mutarotation of salts of Reyckler's acid. V. Comparison of the absorption spectrum of 2-*N*-methylimino-*d*-camphane-10-sulphonic acid with the spectra of other camphane derivatives. R. L. SHRINER and H. SUTHERLAND (J. Amer. Chem. Soc., 1938, 60, 1314—1316; cf. A., 1936, 339).—The ketimine structure of 2-methylimino-*d*-camphane-10-sulphonic acid (modified prep.), m.p. 312—313° (block), [α]_D -137.6° in EtOH, is confirmed by the close resemblance of its absorption spectrum in 95% EtOH (absorption only at <2700 Å.) to that of the 2-*N*-OH-compound and the difference thereof from those of camphor and Reyckler's acid (max. at 2870 Å.). R. S. C.

Myrcenal and myrcenol. R. DELABY and E. DUPIN (Bull. Soc. chim., 1938, [v], 5, 931—938). The products of interaction of myrcene and SeO₂ in EtOH at 80° for 2 hr. and then at 95—96° for 1 hr. are examined. Fractions, b.p. 101—111°/9.5 mm. (*semi-carbazone*, C₁₁H₁₇ON₃, m.p. 168—169°), b.p. 113—116°/17 mm. (2:4-dinitrophenylhydrazones, C₁₆H₁₈O₄N₄, m.p. 129.5—130°), and b.p. 108—113°/11.5 mm. [Ag₂O gives an acid, C₁₀H₁₄O₂ (*Ba* salt)], indicate the presence of an aldehyde, *myrcenal* (I), C₁₀H₁₄O, b.p. 116—119°/17 mm., and some ketones (*myrcenones*). A primary alcohol, *myrcenol*, C₁₀H₁₆O, b.p. 123—128°/17 mm. (*allophanate*, m.p. 110—111°), converted into (I) by SeO₂-EtOH at 93—95° for 1½ hr., and an alcohol, b.p. 140—145°/17 mm., are also obtained. Raman spectra of many fractions are examined; the myrcene skeleton is intact. A. T. P.

Dehydrogenation of triterpene alcohols by means of finely divided copper. K. TSUDA and S. KITAGAWA (Proc. Imp. Acad. Tokyo, 1938, 14, 182—183).—Triterpene alcohols are dehydrogenated (annexed scheme) by heating with Cu as by treating

with CrO₃, but usually with better yield. Thus, heating hederagenin *Me* ester with Cu-bronze at 300° and distilling in vac. gives CH₂O and methylhederagenone, m.p. 203°, [α]_D²⁰ +104.9°, the reaction occurring as shown by the annexed partial formulæ. Soja-



sapogenol-*B* gives similarly the diketone, C₁₉H₄₄O₂ (A., 1938, II, 729). Betulin is, however, unchanged; dihydrobetulin requires repeated distillation to give a small yield of a *keto-aldehyde*, C₃₀H₄₈O₂, m.p. 183—185°, [α]_D²⁵ +11.45° (*dioxime*, decomp. 275°).

R. S. C.

Lignin. D. KRÜGER (Zellstoff u. Papier, 1938, 18, 305—311).—Recent advances in the chemistry of lignin are reviewed. All lignins probably have the same fundamental structure, although their properties vary somewhat with the method of isolation. The aromatic nature of lignin is suggested by the formation of veratric and protocatechuic acids by fusion with alkali, although lignin-carbohydrate complexes appear to be present in nature. D. A. C.

Lignin. XI. Action of amidosulphonic acid on pine wood. H. FRIESE and H. ADEMEIT (Ber., 1938, 71, [B], 1307—1312).—The use of H₂SO₄-Ac₂O-AcOH in the treatment of lignin has the disadvantage that the sulphoacetic acid (I) produced is very difficult to separate from the ligninsulphonic acid. Attempts are therefore made to replace it by NH₂.SO₃H; this reacts rapidly with boiling AcOH-Ac₂O giving NH₄ sulphoacetate, but below 50° the change is much slower than the formation of (I) from H₂SO₄-Ac₂O-AcOH. According to conditions NH₂.SO₃H degrades cellulose (II) to lower sugar acetates or gives sol. complex products containing about 13% of Ac. The reaction between pine wood and NH₂.SO₃H-Ac₂O-AcOH at about 50° proceeds with feeble disengagement of heat but complete dissolution is never attained. The residue is filtered and washed with AcOH and H₂O. The acid solution contains sugar acetates and NH₄OAc. Ultrafiltration of the aq. solution gives a brown residue which is doubtless a lignin-carbohydrate compound. The residue yields to hot H₂O a dark brown powder intermediate in composition between lignin and polysaccharide which does not contain N or S; the undissolved portion (42% of the wood) does not contain N or S and after hydrolysis with NaOMe yields a material with the analytical data of (II). Hydrolysis with 66% H₂SO₄ establishes the presence of >90% of carbohydrates. Treatment of wood with NH₂.SO₃H, therefore, resembles sulphite boiling rather than sulphacetolysis. The lignin is not sulphonated, whereas if it had an aromatic and hence phenolic nature its sulphonation is certain. Further the C content of the so-called lignin substance is ≪ that customary for acid lignin and points rather to the addition of H₂O to a C₉ complex. All the reactions of native lignin (towards

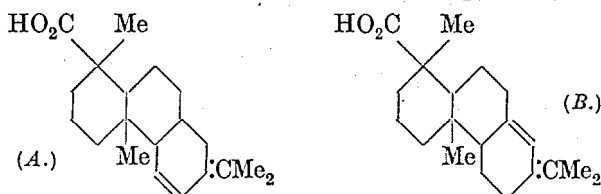
H_2SO_4 , H_2SO_3 , HNO_3 , and $\text{NH}_2\cdot\text{SO}_3\text{H}$) and its behaviour towards conc. mineral acids are not due to an aromatic nature but to an ill-understood at. grouping which is also responsible for the union of lignin in wood with the polysaccharide portions. H. W.

Reaction of hardwood lignin with hydrogen. E. E. HARRIS, J. D'IANNI, and H. ADKINS (J. Amer. Chem. Soc., 1938, 60, 1467—1470).—Lignin, $[\text{C}_{41}\text{H}_{33}\text{O}_7(\text{CO})(\text{OH})_2(\text{OMe})_3]_x$ (80 g.), from *Populus tremuloides* with Raney Ni in dioxan absorbs 1 mol. of H_2 per 25 g. at 260°/300—400 atm., yielding MeOH (22 g.), 4-n-propylcyclohexanol (9 g.), b.p. 92—93°/7 mm. (α -naphthyl-, m.p. 136°, and phenyl-urethane, m.p. 131°; also prepared by H_2 -Raney Ni at 100—200° from $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$), (?) γ -4-hydroxycyclohexylpropyl alcohol (20 g.), b.p. 125—127°/1 mm. [3:5-dinitrobenzoate, m.p. 130—144°; oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ at 65° or $\text{CrO}_3\text{-aq. AcOH-C}_6\text{H}_6$ at room temp. to an acid, $\text{C}_9\text{H}_{14}\text{O}_3$, b.p. about 280°/740 mm., m.p. 55—60° (2:4-, m.p. 80°, and 3:5-dinitrophenylhydrazones, m.p. 90—93°)], 4-n-propylcyclohexane-1:2-diol (3 g.), b.p. 107—110°/1 mm. [*di*-(α -naphthylurethane), m.p. 218—219°; also obtained by hydrogenation (Raney Ni) of 3:4-(OH) $_2$ $\text{C}_6\text{H}_3\cdot\text{COEt}$, prepared from 1:2-OH $\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{COEt}$], a mixture (I) (18 g.), b.p. 130—260°/1 mm., compounds (5 g.), b.p. >260°/1 mm., and intermediate fractions (4 g.). Analysis of (I) indicates the formula $(\text{C}_6\text{H}_{11}\text{O})_n$, n being 3—5; dehydration by Al_2O_3 -pumice in H_2 at 400°, followed by hydrogenation (Raney Ni) at 200°/300 atm., gives hydrocarbons, $\text{C}_n\text{H}_{2n-2}$ or $\text{C}_n\text{H}_{2n-4}$, which from the b.p. (mostly 90—140°/1 atm.) must contain >9C. The presence of units larger than C_9 in lignin is certain. Ether linkings are probable. The relative amounts of the products may be due to the relative ease of hydrogenation and hydrogenolysis and may not indicate differences in structure. Cleavage of C-C linkings is inferred from the large yield of MeOH. The very large absorption of H_2 is noteworthy. R. S. C.

Catic acid. Its preparation, properties, and derivatives. N. L. KALMAN (J. Amer. Chem. Soc., 1938, 60, 1423—1425).—The oleo-resinous exudate ("catico") from *Proripa copaifera*, Griseb., contains 0.5% of H_2O , <2% of volatile oil, and >95% of catic acid and its caticyl ester. The acid, $\text{C}_{20}\text{H}_{34}\text{O}_2$, b.p. 194—195°/1 mm., is obtained by distillation in vac. or dissolution in EtOH, in which the ester is insol. The ester cannot be distilled, but yields, when hydrolysed, caticyl alcohol, $\text{C}_{20}\text{H}_{36}\text{O}$, b.p. 208.5—209.5° (slight decomp.)/4.5 mm. [acetate, b.p. 191° (slight decomp.)/2.5 mm.]. The alkali salts of the acid have detergent action and are pptd. by electrolytes as jellies; other metallic salts are thermoplastic and sol. in hydrocarbons etc. Me, b.p. 200°/1 mm., Et, b.p. 206°/2.5 mm., Bu^a, b.p. 208°/2.75 mm., isoamyl, b.p. 221°/3.5 mm., β -methoxyethyl, b.p. 243°/23 mm., β -hydroxyethyl, b.p. 212°/1.75 mm., and β -butoxyethyl caticate, b.p. 240°/2.5 mm., and triethylene-glycol di-, b.p. 312°/1.5 mm., and glyceryl tri-caticate are described. Cold KMnO_4 converts the acid into dihydroxycatic acid, m.p. 158°, the Me ester, m.p. 64°, of which loses H_2O when heated, yielding an oily ester, $\text{C}_{21}\text{H}_{36}\text{O}_3$. R. S. C.

Dihydroelemolic acid. M. MLADENOVIC (Bull. Soc. Chim. Yougoslav., 1937, 8, 169—174).—The author's contention that the sole product of catalytic hydrogenation of pure elemic acid (I) is dihydroelemolic acid (II), m.p. 238° (A., 1931, 960; 1932, 397), and not a mixture of products, as asserted by Ruzicka (A., 1931, 1067), is confirmed by repetition of previous work; Ruzicka's objections (A., 1933, 69) are thus refuted. Impure (I) yields, apart from (II), only tetrahydro- β -elemonic acid, whereas Ruzicka reported formation of two other acids, in addition to the three dihydroelemolic acids obtained from pure (I). R. T.

Abietic acid. H. RAUDNITZ, N. LEDERER, and E. KAHN (Ber., 1938, 71, [B], 1273—1274).—Ozonisation of abietic acid gives COMe_2 in about 3% yield, whence it appears that about 3% of an impurity of structure A or B is present. To this is probably due



the occurrence of the characteristic absorption max. at 237.5 μ , whereas the main acid possibly shows no absorption in this region. H. W.

Resin acids. Action of palladium on abietic acid. E. R. LITTMANN (J. Amer. Chem. Soc., 1938, 60, 1419—1421).—With 4% Pd-activated Al_2O_3 or 60% Pd-asbestos at 230° Me abietate gives 30—45% of Me dehydroabietate (I), m.p. 60—61° (CNS no. 7—8), which gives an aromatic $(\text{NO}_2)_2$ -derivative, m.p. 192—193°, reduced ($\text{H}_2\text{-Cu-Cr}_2\text{O}_3$ at 150°/133 atm.) to Me diaminodehydroabietate, m.p. 133—134°, which, after diazotisation, couples with $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, R-salt, and PhOH. Abietic acid gives similarly dehydroabietic acid, m.p. 166—167° [converted into (I) by Me_2SO_4], and tetrahydroabietic acid, m.p. 159° (Me ester, b.p. 185—190°/5.7 mm. (CNS no. 5). Fieser's view (A., 1938, II, 108) that disproportionation to an aromatic and reduced acid occurs is thus supported. R. S. C.

Acetylation of Congo copal. E. MERTENS and L. HELINCKX (Congr. Chim. ind. Bruxelles, 1935, 15, II, 813—816; Chem. Zentr., 1936, ii, 1804).—Treatment of transparent Congo copal with $\text{AcOH-Ac}_2\text{O}$ (4:1) for 5 days yields 30% of resinous acetocopal, $\text{C}_{24}\text{H}_{36}\text{O}_4$, m.p. 66°. A. H. C.

Constitution of pectin substances. II. Constitution and gel formation. G. G. SCHNEIDER and H. BOCK (Ber., 1938, 71, [B], 1353—1362; cf. A., 1937, II, 383).—In acid solution the gel is formed of pectin (I) whereas in an alkaline medium (I) suffers rapid removal of the OMe groups with production of insol. pectic acids or their Na salts which are pptd. by Na. The solidity of a (I) gel is a direct function of the mol. size. In addition to mean mol. wt. the proportion of particularly large mols. has an outstanding influence on the elasticity of the gel. In general, the OMe content of pure pectic substances (II) \propto the mol.

wt. Usually the OMe content is determined on a mixture of (II) and pentosans (III) so that the % OMe is only indirectly a measure of the degradation of (II). The separation of (III) and (II) is so tedious that determination of % OMe in (II) has only theoretical interest. Impulse towards gel formation is invariably an elimination of OMe and liberation of CO_2H groups. Since under these conditions a mol. degradation ensues it follows that increase in the rate of gelation is accompanied by decrease in the solidity of the gel. Measurements of the acidity of solutions of (I) with exact control of the mol. size show that on treatment with acid of varied concn. the elimination of OMe is nearly parallel to fission of the mol. If, however, (I) is treated with cold, very dil. NaOH at pH 8–9 OMe is almost completely eliminated within 1 hr. whereas the mol size decreases only very slowly. It is therefore obvious that the CO_2H groups are not concerned with the union of the (I) chains but are free. The parallelism between acidity and OMe content shows that the latter is located at the CO_2H group. The view that (I) is composed of esterified polygalacturonic acids involved with arabinose and galactose must be abandoned in favour of the conception that Me polygalacturonates themselves constitute (I). The nature of the (I) gel is discussed.

H. W.

Snake poisons.—See A., 1938, III, 669.

Pechmann dyes. P. CHOVIN (Ann. Chim., 1938, [xi], 9, 447–553).—A fuller account of work already abstracted (A., 1937, II, 150, 294, 512; 1938, II, 110).

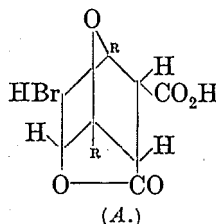
H. W.

Enlargement of ring accompanying dehydration of tetrahydrofurfurylmethylcarbinol. R. PAUL (Bull. Soc. chim., 1938, [v], 5, 919–929; cf. A., 1933, 831).—Dehydration of tetrahydrofurfurylmethylcarbinol over Al_2O_3 (CO_2) at 400° yields mainly 2-methyl- Δ^2 -dihydropyran (I), b.p. $105\text{--}106^\circ/742$ mm. Possible alternative structures are discussed; decomp. of the ozonide, and lability of Br in the bromination products, favour the pyran configuration. Further, aq. mineral acid affords hexan- α -ol- ϵ -one. (I) and H_2 –Pt-black give 2-methyltetrahydropyran, b.p. $104\text{--}106^\circ/770$ mm., converted by HBr – AcOH at 150° into α -dibromohexane, which with NH_2Ph – EtOH forms 1-phenyl-2-methylpiperidine (picrate, m.p. $157\text{--}158^\circ$; cf. isomeric picrate of 1-phenyl-2-ethylpiperidine, m.p. 126°) and with piperidine in CHCl_3 affords 1-pentamethylene-2-methylpiperidinobromide. The results of Connor *et al.* (A., 1936, 340) are discussed.

A. T. P.

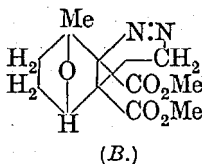
Diene synthesis. V. Steric course of the diene synthesis in the furan series. Diene syntheses of furan and its homologues with acetylenedicarboxylic esters. K. ALDER and K. H. BACKENDORF (Annalen, 1938, 535, 101–113).—The diene syntheses with furan and its homologues proceed normally. As with cyclopentadiene and cyclohexadiene and their derivatives the addition is sterically selective and the adducts have the *endo* configuration. *trans*-*endo*-Oxidohexahydrophthalic acid, m.p. $179\text{--}180^\circ$, is obtained by hydrolysing the Me_2 ester of the corresponding *cis*-acid with saturated KOH – MeOH at 100° . Addition of sylvan to maleic anhydride (I) in Et_2O at

room temp. affords 3 : 6-*endo*-oxido-3-methyl- Δ^1 -tetrahydrophthalic anhydride (II), m.p. 84° (free acid, m.p. $145\text{--}146^\circ$), hydrogenated (Pd – CaCO_3 in EtOAc) to 3 : 6-*endo*-oxido-3-methylhexahydrophthalic anhydride, m.p. $105\text{--}106^\circ$ (corresponding free acid, m.p. 158° , its *Me H* ester, m.p. 118° , and its Me_2 ester, m.p. 76° , converted by alkaline hydrolysis into *trans*-3 : 6-*endo*-oxido-3-methylhexahydrophthalic acid, m.p. $172\text{--}173^\circ$). Very cautious treatment with Br – H_2O at 0°



converts (II) into the bromohydroxy-acid, m.p. 127° , readily transformed by CH_2N_2 in Et_2O into the bromolactone *Me* ester (cf. A), m.p. 151° , whereby its configuration is established. Similarly 3 : 6-*endo*-oxido-3 : 6-dimethyl- Δ^1 -tetrahydrophthalic anhydride, from (I) and 2 : 5-dimethylfuran (III), is transformed into the bromolactonic acid,

m.p. 168° (*Me* ester, $\text{C}_{11}\text{H}_{13}\text{O}_5\text{Br}$, m.p. $155\text{--}156^\circ$), and 3 : 6-*endo*-oxido-3 : 6-dimethylhexahydrophthalic anhydride is converted by boiling MeOH into *Me H* 3 : 6-*endo*-oxido-3 : 6-dimethylhexahydrophthalate, m.p. $106\text{--}108^\circ$, whence the Me_2 ester, m.p. $83\text{--}84^\circ$, hydrolysed by alkali to *trans*-3 : 6-*endo*-oxido-3 : 6-dimethylhexahydrophthalic acid, m.p. $212\text{--}213^\circ$ (decomp.). Me_2 3 : 6-*endo*-oxido- Δ^1 -tetrahydrophthalate is hydrolysed by KOH – MeOH to 3 : 6-*endo*-oxido- Δ^1 -tetrahydrophthalic acid (IV), m.p. $168\text{--}170^\circ$ (*K* salt), and 3 : 6-*endo*-oxido-1-methoxyhexahydrophthalic acid, m.p. $188\text{--}190^\circ$, which is stable towards alkaline KMnO_4 and does not give an anhydride with boiling AcCl . Sylvan and $(\text{C}\text{--}\text{CO}_2\text{Me})_2$ at 100° give the non-cryst. Me_2 3 : 6-*endo*-oxido-3-methyl- Δ^1 : Δ^4 -dihydrophthalate, hydrogenated (Pd – CaCO_3 in EtOAc) to the non-cryst. Me_2 3 : 6-*endo*-oxido-3-methyl- Δ^1 -tetrahydrophthalate, whence the corresponding unsaturated acid (V), m.p. $151\text{--}152^\circ$ (decomp.); this is converted by the prolonged action of an excess of CH_2N_2 into the ester adduct (B), m.p. 95° . $(\text{C}\text{--}\text{CO}_2\text{Me})_2$ and (III) give the non-cryst. Me_2 3 : 6-*endo*-oxido-3 : 6-*dimethyl*- Δ^1 : Δ^4 -dihydrophthalate, reduced to the non-cryst. Me_2 3 : 6-*endo*-oxido-3 : 6-*dimethyl*- Δ^1 -tetrahydrophthalate, whence the free acid, m.p. $173\text{--}174^\circ$ (decomp.), which is unstable towards Na_2CO_3 – KMnO_4 . This with an excess of CH_2N_2 gives the adduct, $\text{C}_{13}\text{H}_{18}\text{O}_5\text{N}_2$ (cf. B), m.p. $78\text{--}79^\circ$. Butadiene (VI) and (IV) at $170\text{--}180^\circ$ give the anhydride (cf. C), m.p. 164° , hydrogenated (Pd – C in EtOAc) to the saturated product, $\text{C}_{12}\text{H}_{14}\text{O}_4$, m.p. $189\text{--}190^\circ$. The adduct, $\text{C}_{13}\text{H}_{14}\text{O}_4$, m.p. $132\text{--}133^\circ$, is derived from (V) and (VI).



H. W.

Derivatives of coumaran. II. Condensation of aliphatic aldehydes and ketones with 5-methoxycoumaran-2-one. Reduction of 5-methoxy-1-isopropylidenecoumaran-2-one. III. O-Acetylation of 5-methoxycoumaran-2-one. R. L. SHRINER and J. ANDERSON (J. Amer. Chem. Soc.,

1938, 60, 1415—1417, 1418—1419; cf. A., 1938, I, 240).—II. 5-Methoxybenz-1:2-dihydrofuran-2-one (I) and the appropriate ketone in HCl-AcOH give $\beta\beta$ -di-5-methoxy-1:2-dihydrobenzofuran-2-onyl-propane, m.p. 209—210°, and -butane, m.p. 194°, and $\gamma\gamma$ -di-5-methoxy-1:2-dihydrobenzofuran-2-onyl-n-pentane, m.p. 231.5—232.5°. By interaction with the appropriate aldehyde, HCl, and ZnCl₂ in hot MeOH are obtained $\alpha\alpha$ -di-5-methoxy-1:2-dihydrobenzofuran-2-onyl-ethane, m.p. 167—168°, -propane, m.p. 135—136°, -n-butane, m.p. 141—142°, and -methane, m.p. 169—170°. With COMe₂ and ZnCl₂ in hot EtOH (I) gives 5-methoxy-1-isopropylidene-1:2-dihydrobenzofuran-2-one, m.p. 141—142°, hydrogenated in presence of PtO₂ at 2—3 atm. in EtOH to the 1-Pr^B ketone, m.p. 75—75.5°, and in presence of Pd-C to 5-methoxy-1-isopropyl-1:2-dihydrobenzofuran, b.p. 149°/19 mm. cycloHexanone gives similarly 5-methoxy-1-cyclohexylidene-1:2-dihydrobenzofuran-2-one, m.p. 146.5—147.5°, reduced (H₂-PtO₂) to 5-methoxy-1-cyclohexyl-1:2-dihydrobenzofuran-2-one, m.p. 86.5—87.5°, but higher aliphatic ketones do not react with (I) under these conditions. M.p. are corr.

III. Although (I) is completely ketonic, giving no colour with FeCl₃ until after 2 hr., it is converted by Ac₂O-AcOH at 100° into 2-acetoxy-5-methoxybenzofuran, m.p. 74—75° (cf. Sonn *et al.*, A., 1922, i, 1164), the structure of which is proved by hydrolysis by very dil. H₂SO₄-EtOH to (I) and by hydrogenation (PtO₂; 2—3 atm.; EtOH) to the 1:2-H₂-compound, which decomposes, when distilled, into 5-methoxybenzofuran and AcOH (identified as piperazonium diacetate).

R. S. C.

Synthesis of coumarins from o-hydroxy-arylalkyl ketones. I. D. CHAKRAVARTI and B. MAJUMDAR (J. Indian Chem. Soc., 1938, 15, 136—138).—2-Methoxy-5-chlorophenyl Et ketone, m.p. 41—42°, obtained from 4-chloro-2-propionylphenol, MeI, and NaOEt-EtOH, yields with CHMeBr·CO₂Et and Zn Et β -hydroxy- β -5-chloro-2-methoxyphenyl- α -methyl- β -ethylpropionate, m.p. 71°, dehydrated by SOCl₂ to Et 5-chloro-2-methoxy- α -methyl- β -ethylcinnamate, b.p. 163°/6 mm., which with HI gives 6-chloro-3-methyl-4-ethylcoumarin, m.p. 94°. 5-Chloro-2-methoxy-4-methylphenyl Et ketone, m.p. 74°, with CHMeBr·CO₂Et similarly yields 6-chloro-3:7-dimethyl-4-ethylcoumarin, m.p. 121°.

A. L.

Coupling of 6-hydroxyflavone with diazo-salts. H. S. MAHAL and K. VENKATARAMAN (Current Sci., 1938, 6, 450).—Na 6-hydroxyflavone with p-NO₂·C₆H₄·N₂Cl and NaOAc gives an orange dye, m.p. 256°. The significance of the reaction is discussed.

A. L.

Natural flavones. I. Constitution of gardenin. P. K. BOSE and R. NATH (J. Indian Chem. Soc., 1938, 15, 139—148).—The formula C₂₁H₂₂O₉ is preferred for gardenin (I), the yellow colouring matter in Dikamali gum from *Gardenia gummifera*, Linn. (I) with Ac₂O gives acetyl-gardenin, m.p. 136°, and with EtOH-KOH yields trimethylgallic acid, and a phenolic substance, C₉H₈O₆, m.p. 158—160°, which when reduced with SO₂ affords a substance, C₉H₁₀O₆, m.p. 175—176°. With HNO₃ (I) yields gardeninone (II), C₂₀H₁₈O₉, m.p. 222—224°, 1:3:4:5-NO₂·C₆H₂(OMe)₃, and

1:2:3:4:5-(NO₂)₂C₆H(OMe)₃. With SO₂ (II) gives gardeninol, C₂₀H₂₀O₉, m.p. 184—185° (Ac₂ derivative, m.p. 146—147°). Since (I) contains 1 OH and 6 OMe and forms a double compound with SnCl₄ in which the ratio Sn/Cl is 1:3, the OH is probably at 5 in a flavone nucleus. (I) is either 5-hydroxy-3:6:8:3':4':5'- or -3:7:8:3':4':5'-hexamethoxyflavone.

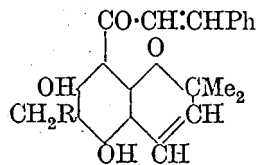
A. L.

Synthesis of wogonin [5:7-dihydroxy-8-methoxyflavone]. R. C. SHAH, C. R. MEHTA, and T. S. WHEELER (Current Sci., 1938, 6, 503).—Condensation of 2:4-dihydroxy-3:6-dimethoxyacetophenone (Baker *et al.*, A., 1929, 326) with NaOBz and Bz₂O yields 7-hydroxy-5:8-dimethoxyflavone. HI converts this into 5:6:7-trihydroxyflavone, and AlCl₃ into a trihydroxyflavone, m.p. 251—252°, or under mild conditions into wogonin (Hattori, A., 1931, 493).

A. Li.

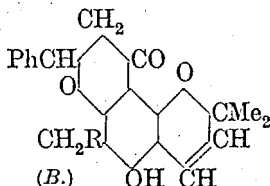
Rottlerin. H. BROCKMANN and K. MAIER (Annalen, 1938, 535, 149—175; cf. A., 1937, II, 429; 1938, II, 108).—Rottlerin (I), m.p. 201—202° (Berl), is C₃₀H₂₈O₈. It contains four active H (Zerevitinov-Roth) and when treated with O₃-KMnO₄ gives 0.2 mol. of COMe₂ indicating the presence of Pr^B or gem-Me. It gives a penta-acetate, m.p. 211.5—212.5°. With CH₃N₂ (I) yields a Me₂ ether (II), m.p. 245—246° (decomp.), converted into a Me₅ ether (III), C₃₀H₂₃O₃(OMe)₅, m.p. 142.5°, identical with the compound C₂₇H₂₂O₃(OMe)₄ of Ray *et al.* Hydrogenation (Pd-C in COMe₂) of (I) affords tetrahydrorottlerin (IV), C₃₀H₃₂O₈, m.p. 211° (penta-acetate, m.p. 188°). Similarly (II) affords tetrahydrorottlerin Me₂ ether, m.p. 193—194°, also obtained by methylation of (IV) and transformed by Me₂SO₄ and K₂CO₃ in boiling COMe₂ into tetrahydrorottlerin Me₅ ether, m.p. 108—108.5°, also obtained by hydrogenation of (III). Treatment of (I) with H₂O₂ in alkaline solution gives CHPh·CH·CO₂H whilst PhCHO is obtained by degradation with O₃ or when (I) is boiled with dil. NaOH, thus disclosing the presence of the CHPh·CH· group. The formation of o- or p-C₆H₄(CO₂H)₂ by the oxidation of (I) could not be confirmed. Diazoaminobenzene and (I) in boiling EtOH gives 2:4:6-trihydroxy-3-acetyl-5-methylazobenzene, m.p. 206°, which contains 2—3 active H (Zerevitinov-Roth) and gives 1.6 mols. of AcOH when oxidised by CrO₃ (Kuhn-Roth); it is obtained synthetically from methylphloracetophenone (V), m.p. 213—214°. (Analogously, methylphlorpropiophenone, m.p. 205°, is transformed into 2:4:6-trihydroxy-3-propionyl-5-methylazobenzene, m.p. 211°.) (V) is also obtained by the thermal decomp. of (I). Very prolonged treatment of (I) with boiling EtOH leads to isorottlerin (VI), C₃₀H₂₈O₈, m.p. 180°, the production of which is accelerated by H₃PO₄ or d-camphorsulphonic acid, also obtained in boiling PhMe or, preferably, in boiling AcOH. It contains 2—3 active H and yields 0.48 mol. of COMe₂ when degraded by O₃-KMnO₄. Acetylation and methylation give only amorphous or oily products. Hydrogenation (Pd-C in COMe₂) of (VI) gives dihydroisorottlerin, m.p. 210—211°, so that the isomerisation of (I) is accompanied by the loss of a double linking; if this is absent, as in (IV), isomerisation does not take place. In contrast with (I), (VI) does not yield a dye

when treated with $\text{NPh}\cdot\text{N}\cdot\text{NPh}$ although the presence of a methylphloracetone residue is betrayed by the formation of (V) by the thermal decomp. of (VI). The presence of the Ph residue of the $\text{CHPh}\cdot\text{CH}\cdot$ group is established by the formation of BzOH but the residue $\text{CHPh}\cdot\text{CH}$ is not present as such since PhCHO is not formed by ozonolysis. To (I) and (VI) the constitutions A and B respectively are ascribed.



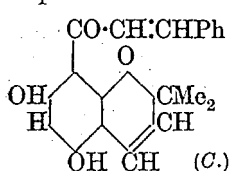
(A.)

[R = 2 : 4 : 6 : 3 : 5-(OH)₃C₆AcMe.]



(B.)

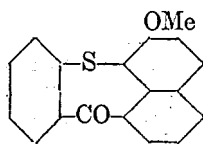
These are in harmony with the reactions described above and with the absorption spectra of (I) and (VI) in CHCl_3 . (II), like (IV), is not isomerised by boiling AcOH . This may be due to the etherification of OH required for ring closure or to the diminished activity of (II). It does not appear possible to convert 2-hydroxy-4 : 6-dimethoxy-3-methylchalcone, m.p. 142°, or 2-hydroxy-4 : 6 : 4'-trimethoxy-3-methylchalcone into the corresponding flavanones by the prolonged action of AcOH . Attempts to transform (I) by *d*-camphorsulphonic acid into an optically active flavanone derivative led only to optically inactive (VI). Rottlerone, to which the constitution C is ascribed, is dissolved by boiling AcOH with marked lightening of colour but does not appear to give well-defined products. With boiling AcOH-HI (IV) gives a substance, $\text{C}_{30}\text{H}_{30}\text{O}_7$, m.p. 169—170°, which has not been completely investigated.



(C.)

H. W.

New ring systems. V. Phenyl 2-methoxy-8-naphthyl ketone o : 1-sulphide. W. KNAPP (Monatsh., 1938, 71, 440—443; cf. A., 1938, II, 59).—1 : 2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{OMe}$ and $\text{o-SH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ with anhyd. K_2CO_3 and Cu powder in boiling $n\text{-C}_5\text{H}_{11}\cdot\text{OH}$ give 2-carboxyphenyl 2'-methoxy-1'-naphthyl sulphide, m.p. 226—228°, which with P_2O_5 in boiling PhMe yields the 1 : 8-cyclic sulphide ketone (I), m.p. 184—185°. Similarly from 1- $\text{C}_{10}\text{H}_7\text{Br}$ is formed 2-carboxyphenyl 1'-naphthyl sulphide, m.p. 213—215°, which with $\text{P}_2\text{O}_5\text{-PhMe}$ yields 3 : 4-benzthioxanthone, m.p. 193—194°.



(I.)

J. D. R.

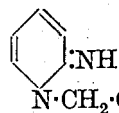
Pyrrole-indole group. Series II. XXIII. Derivatives of pyrrole-1- and -2-carboxylic acid. B. ODDO and C. ALBERTI (Gazzetta, 1938, 68, 204—214).—The K derivative of pyrrole (I) and CS_2 in PhMe yield K pyrrole-1-dithiocarboxylate (II) (Cu, Hg, Ag, and Pb salts described), which with dil. H_2SO_4 gives the oily acid (III); this is very unstable, and spontaneously oxidises to bis-1-pyrrylthiocarboxyl disulphide, ($\text{C}_4\text{H}_4\text{N}\cdot\text{CS}\cdot\text{S}$), m.p. 95—96° (decomp.). With EtI in EtOH , and with PhN_2Cl in aq. EtOH , (II) gives the Et, b.p. 162—164°/33 mm., and Ph, b.p.

180—200° (bath)/30 mm. (decomp. to Ph_2S , Ph_2S_2 and a product, m.p. 147—148°) esters of (III). $\text{C}_4\text{H}_3\text{NH}\cdot\text{CS}_2\text{MgBr}$ (IV), from the MgBr derivative of (I) and CS_2 , with EtI yields Et pyrrole-2-dithiocarboxylate, b.p. 60°/60 mm., and, with AcCl , S-acetylpyrrole-2-dithiocarboxylic acid, $\text{C}_4\text{H}_3\text{NH}\cdot\text{CS}\cdot\text{S}\cdot\text{Ac}$, m.p. 87—88°. The K derivative of 2 : 5-dimethylpyrrole with CS_2 forms K 2 : 5-dimethylpyrrole-1-dithiocarboxylate (Ag, Cu, Ni, Co, and Pb salts), which with PhN_2Cl gives the Ph ester, and with dil. H_2SO_4 gives the unstable acid, rapidly oxidised to bis-2 : 5-dimethyl-1-pyrrylthiocarboxyl disulphide, m.p. 177—178° (decomp.). E. W. W.

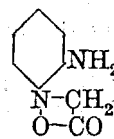
Molecular compounds of pyrrole derivatives. II. M. DEŽELIĆ (Bull. Soc. Chim. Yougoslav., 1937, 8, 145—156).—The fusion diagrams of the systems Et 2 : 4-dimethylpyrrole-5-carboxylate (I)— CHPh_3 , — $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$, and —quinine, and Et 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate (II)— $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, — PhOH , —*m*-, —*o*-, and —*p*- $\text{C}_6\text{H}_4(\text{OH})_2$, —salicylic acid, and — CHPh_3 do not suggest compound formation. 1 : 1 compounds are described in the systems (I)— $\text{CCl}_3\cdot\text{CO}_2\text{H}$, transition point 35.5°, (II)— $\text{CCl}_3\cdot\text{CO}_2\text{H}$, transition point 79°, and (II)—picric acid, m.p. 107.2°. R. T.

Reaction between amines and unsaturated compounds containing halogen attached to one of the ethylenic carbon atoms. II. Preparation and constitution of some new diamines. J. C. ROBERTS (J.C.S., 1938, 963—965; cf. A., 1936, 1236).— $\text{CHMe}\cdot\text{CCl}\cdot\text{CO}_2\text{Et}$ and piperidine in EtOH yield Et $\alpha\beta$ -dipiperidinobutylate, b.p. 181—183°/14 mm. $\text{CHPh}\cdot\text{CBr}\cdot\text{CO}_2\text{Et}$ with piperidine yields Et $\alpha\beta$ -dipiperidino-, m.p. 74—75° (dihydrochloride readily loses HCl ; picrate, m.p. 122—123°), and with NHMe_2 gives Et $\alpha\beta$ -bis(dimethylamino)- β -phenylpropionate, b.p. 154—155°/8 mm., solidifying after several months, m.p. 37—38° [platinichloride, m.p. 185° (decomp.); dihydrochloride; picrate, m.p. 148—149°], which when boiled with aq. KOH yields some NHMe_2 , and with dil. H_2SO_4 gives a mixture of phenylglycidic acid and $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ (formed by the action of H_2SO_4 on the former). A. LI.

Pyridinium compounds and betaines. A. KIRPAL and B. WOJNAR (Ber., 1938, 61, [B], 1261—1266).—Pyridylglycine (I) is converted by boiling, dil.



(A.)

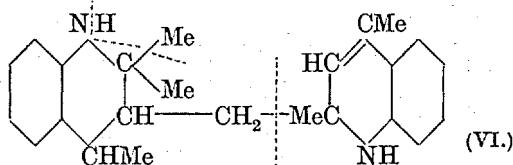


(B.)

aq. alkali or by HNO_2 into pyrid-2-oneacetic acid, thus establishing the constitution A or B. With warm conc. alkali hydroxide (I) yields Na 2-iminopyridineacetate. $\text{C}_5\text{H}_5\text{N}$ and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ afford the compound $\text{C}_5\text{H}_5\text{N}(\text{Cl})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 160°, which decomposes when heated into $\text{C}_5\text{H}_5\text{N}$, HCl and $\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$. It is transformed by Ag_2O into the very hygroscopic 1- β -carboxyethylpyridinium hydroxide, m.p. 90°. 2-Hydroxy-1- β -carboxyethylpyridinium chloride, m.p. 96°, is decomposed by boiling aq. alkali into $\text{OH}\cdot\text{C}_5\text{H}_4\text{N}$, and $\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$. 3-Hydroxy-1- β -carboxyethylpyridinium chloride, m.p. 183°, is converted by NaOH into 3-hydroxy-1- β -carboxyethylpyridinium hydroxide, m.p. 184° or (+1H₂O), m.p.

180°, which when heated above its m.p. passes partly into 3-OH-C₅H₄N and CH₂:CH-CO₂H but mainly yields the anhydride. 4-Hydroxy-1-β-carboxyethylpyridinium chloride has m.p. 196°. 2-Aminopyridine and CH₂Cl-CH₂-CO₂H at 100° afford 2-amino-1-β-carboxyethylpyridinium chloride, decomp. 285°, which with moist Ag₂O yields 2-amino-1-β-carboxyethylpyridinium hydroxide, m.p. 156° (decomp.); this loses H₂O at 120° with formation of pyridone-2-imide-propionic acid, which slowly absorbs 1H₂O when exposed to air. H. W.

Reaction of acetone with aniline. D. CRAIG (J. Amer. Chem. Soc., 1938, 60, 1458—1465).—NH₂Ph, COMe₂, and a trace of HCl at 100° give 68% of "acetoneanil" (I), m.p. 26—27°, b.p. 255—260°/743 mm. (slight decomp.) (hydrochloride, m.p. 214—216°, partly hydrolysed by H₂O) (cf. Reddell and Thurm, A., 1932, 1142), and 31% of a resin. At 120—150° NHPH₂ is the main by-product, but under other conditions (*p*-NH₂·C₆H₄)₂CMe₂ (II), *p*-C₆H₄Pr⁶NH₂, phenyl-*p*-cumylamine (III), m.p. 70—72° (*Ac* derivative, m.p. 94—95°), 5:5-dimethylacridane (IV), 5-methylacridine, 2:4-dimethylquinoline (V), and polymeric quinoline derivatives are obtained. The structure of (I) as 2:2:4-trimethyl-1:2-dihydroquinoline is probable (cf. *loc. cit.*), but 2:4:4-trimethyl-1:4-dihydroquinoline is also a possibility. With conc. HCl (0.1 mol.) at 100° (I) gives a dimeride, b.p. 215—220°/2.5 mm. (*Ac*₂ derivative, m.p. 185—186°), believed to be (VI), and higher



polymerides; these products are depolymerised by Cu-Cr₂O₃ or by distilling in vac. with a trace of a strong acid, and are converted by H₂-Raney Ni into the H₂-derivative of (I). 2:4-Dimethylquinoline methiodide, new m.p. 263—265° (decomp.), and MgMeI give the *N*-Me derivative, b.p. 105—115°/1.5 mm. (zincchloride, m.p. 195—197°; picrate, m.p. 147—148°), of (I). Acid decomp. (NH₂Ph, HCl at the b.p.) of (I) gives (V) and 2:3:4-trimethylquinoline (VII), m.p. 91—92°, probably by way of (VI), which decomposes by fission along the broken lines; this view is supported by the fact that (VII) is obtained with C₂H₆ by the action of HCl at 200—215° on the "anil" from COMeEt; this anil is probably 2:3:4-trimethyl-2-ethyl-1:2-dihydroquinoline. (V) is best (86% yield) obtained from (I) by NaNH₂ (0.5 mol.) at 150—210°, about 1 mol. of CH₄ being liberated; this reaction does not occur by way of (VI), since (VI) gives <0.5 mol. of CH₄ at a much higher temp. The H₂-derivative of (I) is stable to NaNH₂. 6:6'-Methylenebis-2:2:4-trimethyl-1:2-dihydroquinoline is obtained from (I) and CH₂O, having m.p. 153—154°. The formation of NHPH₂ from NH₂Ph, COMe₂, and HCl probably occurs by way of (II) thus: (II) + 2NH₂Ph → 2NH₃ + (*p*-NHPH·C₆H₄)₂CMe₂ (VIII) → NHPH₂ + *p*-NHPH·C₆H₄·CMe:CH₂ (IX); (IX) with 2NH₂Ph then re-forms (VIII). In confirmation

of this view, 1 mol. of (II) with 8 of NH₂Ph and 5 of NH₂Ph, HCl at about 195° give 2.2 mols. of NHPH₂ with some (III) and (V). ββ-Di-*p*-anilinodiphenylpropane (VIII), m.p. 99—100°, is obtained (a) from NHPH₂, COMe₂, and conc. HCl at 120—135°, (b) with NH₂Ph and (IV) from (II) (0.1), NHPH₂ (0.5), and NHPH₂, HCl (0.1 mol.) at about 240°, and (c) from (II), *o*-C₆H₄Cl-CO₂H, K₂CO₃, and a trace of CuI at 150—170°. However, at 160—170° COMe₂, NHPH₂ (large excess), and HCl give *p*-isopropenyldiphenylamine (IX), m.p. 91—92°, best obtained by distilling (VIII) in a vac. with a little H₃PO₄; at 250—259° 60% of (IV) is formed, with some 5-methylacridine, acridine, and (III), the formation of (III) indicating that (IX) is an intermediate. Attempts to obtain (VIII) directly from COMe₂, NH₂Ph, and HCl failed. R. S. C.

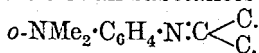
Formation and destruction of histamine by ascorbic acid and thiol compounds. P. HOLTZ and R. HEISE (Arch. exp. Path. Pharm., 1937, 187, 581—588).—Histamine (I) was formed from histidine (II) by addition of ascorbic acid or cysteine by slow oxidation in the air, but not in an O₂ atm. A min. concn. of (II) was necessary to obtain (I). Formation of (I) was inhibited by Fe (cf. A., 1937, III, 210).

I. S.
Formation of histamine from histidine by oxido-reductive catalytic processes. P. HOLTZ (Arch. exp. Path. Pharm., 1937, 187, 589—593).—Histamine (I) was formed in aq. solutions of histidine when alternately perfused with O₂ (½ min.) and H₂ (2 min.) in presence of Pd. Less or no (I) was formed when perfusion with O₂ was of longer duration than that with H₂. I. S.

Synthesis of umbellulonic acid. P. C. GUHA and M. S. MUTHANNA (Current Sci., 1938, 6, 449).—Diazoacetone with CH₂:CPr⁶·CO₂Et gives 5-carbethoxy-3-acetyl-5-isopropylpyrazoline, b.p. 130—135°/3 mm., which when heated to 180° loses N₂ giving the *Et* ester, b.p. 233—235°/685 mm., of *cis*-umbellulonic acid (oxime, m.p. 145—146°; semicarbazone, m.p. 170°), oxidised to *cis*-umbellularic acid. A. LI.

Alloxandimethylaminoanil. Constitution of the dinuclear compounds of alloxan with aromatic *o*-diamines. H. RUDY and K. E. CRAMER (Ber., 1938, 71, [B], 1234—1242).—*o*-NMe₂·C₆H₄·NH₂, obtained by reduction (H₂-Pd-CaCO₃ in MeOH) of *o*-NMe₂·C₆H₄·NO₂, readily condenses with alloxan (I) in boiling EtOH-H₂O to alloxan-5-*o*-dimethylaminoanil (II), CO<NH·CO>C·N·C₆H₄·NMe₂-*o*, m.p. 248° when brought into bath at 220° and then rapidly heated or decomp. without melting at >300° when slowly heated. The properties of (II) resemble so closely those of the compounds obtained by condensing (I) with *o*-C₆H₄(NH₂)₂ and *o*-NH₂·C₆H₄·NHMe, respectively, that there can be no doubt that all are anils and that Hinsberg's formulation N:C(OH)N≡C·CO·NH·CO·NH₂ is incorrect. (I) is amphoteric, being sol. in warm aq. Na₂CO₃ and yielding a hydrochloride, m.p. 236° (decomp.), stable only in presence of an excess of acid. In conc. H₂SO₄ it

gives a colourless solution. In conc. NaOH (I) gives a sparingly sol. Na salt but NH_3 is readily evolved with production of *o*-dimethylaminoanilomalonicimide, $\text{o-NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{NH}$, m.p. 239° (decomp.). This is stable towards 50% NaOH and hot conc. HCl. With CH_2N_2 it affords the corresponding methylimide, m.p. 156—157° (picrate, m.p. 133°), which is devoid of acid properties. (II) is a powerful reducing agent, pptg. Ag from AgNO_3 and giving a red dye in boiling $\text{C}_5\text{H}_5\text{N}$, best after addition of H_2O_2 . With H_2O_2 in dil. HCl it gives an intense violet colour which becomes yellow-green on warming; this appears characteristic of all substances with the group,



H. W.

Formula of indigotin. J. VAN ALPHEN (Chem. Weekblad, 1938, 35, 435—439).—The various formulae for indigotin are discussed. Its colour, stability and the influence of various substituents are explained by its being a resonance-hybrid of at least six different structures.

S. C.

Glyoxaline group. VII. Opening of the benziminazole ring. B. ODDO and (SIGNA.) L. RAFFA (Gazzetta, 1938, 68, 199—204).—The MgBr derivative of benziminazole (I) with Pr^iCOCl (II) in Et_2O gives 1-butyrylbenziminazole (II) (A., 1933, 285), not altered by boiling with (II). With boiling $(\text{EtCO})_2\text{O}$, (I) yields its 1-EtCO derivative, and *o*-dipropionamidobenzene, m.p. 130°. Similarly $(\text{Pr}^i\text{CO})_2\text{O}$ gives (II) and *o*-dibutyramidobenzene, m.p. 132°. E. W. W.

Synthesis of quinazolines (and benzoglyoxalines). V. A. AHMED, K. S. NARANG, and J. N. RAY (J. Indian Chem. Soc., 1938, 15, 152—159).—*o*-Nitrochloroacetanilide and piperidine in C_6H_6 give *o*-nitro- ω -piperidinoacetanilide, m.p. 83°, reduced by Zn-HCl to *o*-amino- ω -piperidinoacetanilide, m.p. 173°; this with AcOH-NaOAc gives 2-piperidinomethylbenziminazole, m.p. 201°. Similarly *o*-nitro- ω -diethylaminoacetanilide, m.p. 70°, affords *o*-amino- ω -diethylaminoacetanilide, m.p. 81°, ring-closure of which yields 2- α -diethylaminomethylbenziminazole, m.p. 169°, and *o*-nitro- β -chloropropionanilide, m.p. 85° gives *o*-nitro- β -piperidinopropionanilide, m.p. 44°, leading to *o*-amino- β -piperidinopropionanilide, m.p. 110. Ring-closure of this substance, however, gave a polymeride, m.p. 290°, of 2-vinylbenziminazole (I). *o*-Nitro- β -diethylaminopropionanilide is reduced to *o*-amino- β -diethylaminopropionanilide, m.p. 56°, which on ring-closure also affords (I). For the synthesis of quinazolines, *o*-aminobenzamide is condensed with $\text{CH}_2\text{Cl} \cdot \text{COCl}$ or $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{COCl}$ and the products are condensed with NHEt_2 or piperidine and treated with KOH to give the quinazoline. The following are prepared: *o*- ω -chloroacetamidobenzamide, m.p. 171°, *o*- α -piperidinoacetamidobenzamide, m.p. 186°; 2-piperidinomethyl-, m.p. 170°, and 2- α -diethylaminomethyl-quinazol-4-one, m.p. 85°; *o*- β -piperidinopropionamidobenzamide, m.p. 140°, 2- β -piperidinoethyl-quinazol-4-one, m.p. 148°, *o*- β -diethylaminopropionamidobenzamide, m.p. 99°, 2- β -diethylaminoethylquinazol-4-one, m.p. 122°, 6-nitro-N-3:4-methylenedioxybenzylphthalimide, m.p. 218°, 6-nitro-3:4-methylene-

dioxybenzylamine, m.p. 105°, 6-nitro-, m.p. 204°, and 6-amino-3:4-methylenedioxyacetbenzylamine, m.p. 126° (ring-closure of this substance could not be effected), N-6-nitro-3:4-methylenedioxybenzylsuccinimide, m.p. 175°; methylenedioxyisovasicone (II), m.p. 267°.

A. L.

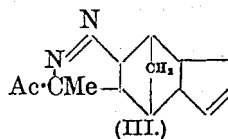
Chemiluminescent organic compounds. VI. Isolation of peroxide derivatives of phthalaz-1:4-diones. H. D. K. DREW and R. F. GARWOOD (J.C.S., 1938, 791—793).—The Na salt of 5-amino-phthalaz-1:4-dione in H_2O_2 gives the Na salt of 5-amino-1:4-dihydroxy-2:3-dihydrophthalazine peroxide ($+\text{H}_2\text{O}$); the Ba salt of 1:4-dihydroxy-2:3-dihydrophthalazine peroxide is similarly obtained. These are chemiluminescent and are probable intermediates in the luminescing reactions of the diones. By the use of duroquinol, atm. O_2 may be used in these reactions of the diones.

F. R. S.

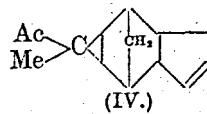
Stereochemistry of diphenyls. XLV. Stereoisomeric dipyrroldiphenyls. R. ADAMS and R. M. JOYCE, jun. (J. Amer. Chem. Soc., 1938, 60, 1491—1492).— $\text{CH}_2\text{Ac} \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$ (I) and benzidine in AcOH at 100° give 4:4'-bis-(3-carbethoxy-2:5-dimethyl-1-pyrroldiphenyl, m.p. 182—183°, which could not be smoothly hydrolysed. NaOAc, *o*-tolidine, and (I) in hot AcOH give 4:4'-bis-(3-carbethoxy-2:5-dimethyl-1-pyrroldiphenyl, (?) dl., m.p. 172—174°, and (?) meso-form, m.p. 142—144°. Dianisidine similarly gives 3:3'-dimethoxy-4:4'-bis-(3-carbethoxy-2:5-dimethyl-1-pyrroldiphenyl, forms, m.p. 185—187° and 168—170°, respectively. M.p. are corr.

R. S. C.

Diene syntheses. XXXI. Behaviour of azibutanone towards unsaturated systems. O. DIELS and H. KÖNIG (Ber., 1938, 71, [B], 1179—1185).—Azibutanone (I) does not react with aliphatic dienes or with monomeric cyclopentadiene. With $(\text{C} \cdot \text{CO}_2\text{Et})_2$ in abs. Et_2O it affords *Et*, 3-acetyl-3-methylpyrazole-4:5-dicarboxylate, b.p. 180—181°/13 mm. (corresponding Me_2 ester, m.p. 65°), hydrolysed by KOH-MeOH to 3-methylpyrazole-4:5-dicarboxylic acid ($+\text{H}_2\text{O}$) (II), m.p. 239° (decomp.) [*Et* H ester, m.p. 213° (decomp.)]. (II) is oxidised ($\text{KMnO}_4\text{-Na}_2\text{CO}_3$) to pyrazole-3:4:5-tricarboxylic acid (III), m.p. 234°, identified by conversion into Me_3 1-methylpyrazole-3:4:5-tricarboxylate, m.p. 100°, obtained also from $\text{CHN}_2 \cdot \text{CO}_2\text{Et}$ and $(\text{C} \cdot \text{CO}_2\text{Et})_2$. Distillation of (III) with CaO give pyrazole. Dicyclopentadiene and (I) at 80° afford the adduct (III) (semicarbazone, m.p. 218°), which when distilled under 13 mm. gives a liquid ketone (IV), b.p. 155—158°/13 mm. (semicarbazone, m.p. 254°), and is hydrogenated (PtO_2 in EtOAc) to the corresponding saturated ketone, b.p.



(III.)



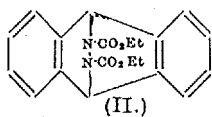
(IV.)

148—150°/13 mm. (semicarbazone, m.p. 218°). Pyrrole and (I) in presence of Cu powder give 2-isobutyryl-

pyrrole (V), m.p. 85°. 5-isoButyryl-2-methylpyrrole, m.p. 106°, converted by Br in AcOH into 3:4-dibromo-5-isobutyryl-2-methylpyrrole, m.p. 162°, and 5-isobutyryl-2:4-dimethylpyrrole, m.p. 114°, are obtained similarly. The constitution of (V) is established by its formation from $\text{Pr}^{\text{B}}\text{COCl}$ and Mg pyrrol iodide. Et_2 azodicarboxylate and (I) vigorously give Et_2 acetylmethylhydrazomethanedicarboxylate, $\text{C}(\text{AcMe})\text{N}(\text{CO}_2\text{Et})_2$, b.p. 180—184°/14 mm., m.p. 44—46°, readily converted into Ac_2 and $(\text{NH}\cdot\text{CO}_2\text{Et})_2$.

H. W.

Diene syntheses. XXXII. Anthracene and azodicarboxylic ester. O. DIELS, S. SCHMIDT and W. WITTE (Ber., 1938, 71, [B], 1186—1189).—Anthracene (I) and $(\text{N}\cdot\text{CO}_2\text{Et})_2$ in boiling PhMe give the labile adduct (II), m.p. 138°, hydrolysed (KOH—MeOH or EtOH) to K_2CO_3 and (I) and thermally decomposed into its components.

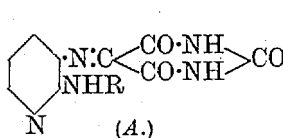


It is converted by dil. HCl in lukewarm AcOH or by HCO_2H at room temp. into the stable adduct, (?) 9:10-dicarbethoxylaminoanthracene, m.p. 242°, which could not be satisfactorily hydrolysed. Similarly, $(\text{N}\cdot\text{CO}_2\text{Me})_2$ affords a labile adduct, $\text{C}_{18}\text{H}_{16}\text{O}_4\text{N}_2$, m.p. 192°, thermally decomposed into its components and transformed by acid into the stable (?) 9:10-dicarbomethoxylaminoanthracene, m.p. 267°, which is very resistant towards hydrolysis. H. W.

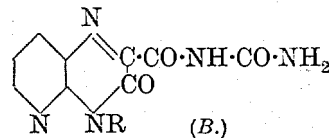
Synthesis of compounds related to 2'-phenyl-3':4':2:3-quinolinoquinoline. J. MOSZEW (Bull. Acad. Polonaise, 1938, A, 98—115).—4-Anilo-2-phenyl-3':4':2:3-quinolino-4-quinolone (I), m.p. 245—246° [picrate, m.p. 245° (decomp.); hydrochloride, m.p. 252° (decomp.); nitrate, m.p. 137—138° (decomp.)], a by-product in the reaction of COPhMe with $\text{CS}(\text{NHPh})_2$ (A., 1932, 1039), is hydrolysed by EtOH—HCl to the corresponding quinolone, m.p. 365° (hydrochloride and nitrate lose acid at >200° and melt at 365°), or by EtOH—KOH under pressure to 4-hydroxy-2'-phenyl-3':4':2:3-quinolinoquinoline, m.p. 324—325° [picrate, m.p. 240° (decomp.); hydrochloride, m.p. 275° (decomp.)]. The latter is converted by HCl into the quinolone, whilst EtOH—KOH effects the reverse process. Either isomerise when heated with Zn dust yields 2'-phenyl-3':4':2:3-quinolinoquinoline, m.p. 300—301° [hydrochloride, loses HCl at >200°, m.p. 300°; picrate, m.p. 260—261° (decomp.)], also obtained by heating 4-anilino-2-phenyl-3-methylquinoline (A., 1933, 956) with Zn dust, an intermediate product being 2'-phenyl-1:4-dihydro-3':4':2:3-quinolinoquinoline, m.p. 202° [hydrochloride, m.p. 240° (decomp.); picrate, m.p. 265—266° (decomp.)]. With dil. HNO_3 , (I) is partly oxidised to N-phenyl-2:3:4-diquinolinoquinoline, m.p. 245° [nitrate, m.p. 152° (decomp.); picrate, m.p. 280° (decomp.)]. Reduction of (I) ($\text{Zn}\text{--}\text{AcOH}$) yields 4-anilino-2'-phenyl-1:4-dihydro-3':4':2:3-quinolinoquinoline (II), m.p. 210°, giving the following derivatives: hydrochloride, m.p. 360° (decomp.); nitrate, m.p. 175° (decomp.); picrate, m.p. 257° (decomp.); N-NO-derivative acetate, m.p. 219—220° (decomp.); N-Ac derivative, m.p. 301—302°; methosulphate, m.p. 247° (decomp.); methiodide, m.p. 255° (decomp.), hydrolysed by EtOH—KOH to

4-anilino-2'-ethoxy-2'-phenyl-1'-methyl-1:4-dihydro-3':4':2:3-quinolinoquinoline, m.p. 105—106° (decomp.) [picrate, m.p. 278—279° (decomp.)], which with HCl yields the methochloride, m.p. 220° (decomp.), of (II). (II) is hydrolysed by EtOH—KOH to the 4-OH-compound. Both this and the isomeric ketone are reduced ($\text{Na}\text{--}\text{C}_5\text{H}_{11}\cdot\text{OH}$) to the 1':2':3':4'-tetrahydro-ketone, m.p. 308—309° [picrate, m.p. 224° (decomp.)]. A. Li.

Dinuclear alloxan derivatives of 2:3-diaminopyridines. H. RUDY and O. MAJER (Ber., 1938, 71, [B], 1323—1332).—2-Chloro-3-aminopyridine is converted by 33% NHMe_2 and CuSO_4 at 170° into the very unstable 3-amino-2-dimethylaminopyridine, b.p. 110—111°/12 mm., m.p. (indef.) 60° (hydrochloride, m.p. 202°; picrate, m.p. 139°), which with alloxan (I) in dil. HCl gives a very small yield of the compound, $\text{C}_{15}\text{H}_{13}\text{O}_7\text{N}_7$ or $\text{C}_{15}\text{H}_{15}\text{O}_8\text{N}_7$, m.p. 308°. 3-Amino-2-propylaminopyridine (II) and (I) in boiling dil. AcOH afford the yellow alloxan-2-propylamino-3-pyridylimide (cf. A), m.p. 243° (decomp.) when brought into bath at 200°, whereas in H_2O , MeOH, or EtOH the product is 2-keto-1-propyl-1:2-dihydro-8-azaquinoxaline-3-carboxureide (III) (cf. B), m.p. 243° (decomp.) when



(A.)



(B.)

introduced into a bath at 200° and then rapidly heated. Boiling 20% Na_2CO_3 or short treatment with 10% NaOH does not affect (III) whereas with boiling 30% NaOH it affords (II). Alloxan-2-methylamino-3-pyridylimide, m.p. 235—236° (decomp.), is somewhat more stable than the Pr derivative and can be crystallised at will from AcOH. It is isomerised by boiling 20% Na_2CO_3 or by 2N-NaOH at room temp. to 2-keto-1-methyl-1:2-dihydro-8-azaquinoxaline-3-carboxureide, m.p. 239° (decomp.), also obtained from 3-amino-2-methylaminopyridine (IV) and (I) in dil. HCl; it is stable towards Na_2CO_3 but decomposed by 30% NaOH with formation of (IV). 2:3-Diaminopyridine and (I) give alloxan-2-amino-3-pyridylimide, m.p. 280—285° (Na salt), whence 2-hydroxy-8-azaquinoxaline-3-carboxureide, m.p. 306° (decomp.) when rapidly heated, converted by short treatment with boiling 4N-NaOH into 2-hydroxy-8-azaquinoxaline-3-carboxylic acid, m.p. 235°. H. W.

Synthesis of 5-5'-5'-phenylhydantoinyl-5-ethylbarbituric acid. S. L. RUSKIN and M. PFALZ (J. Amer. Chem. Soc., 1938, 60, 1471—1472).—Prep. of OH-CHPh-CN and therefrom of 5-phenylhydantoin and its 5-Br-derivative (I) is modified to give 86, 90, and 37% yield, respectively. Na 5-ethylbarbiturate and (I) in AcOH at room temp. give 5-5'-5'-phenylhydantoinyl-5-ethylbarbituric acid, m.p. 215—218°.

R. S. C.

Nucleic acids. IX. Preparation of adenosine. H. BREDERECK (Ber., 1938, 71, [B], 1013—1014).—Adenosine picrate (A., 1938, III, 343) suspended in warm H_2O is treated with KOH and the solution is cooled to room temp. and then to 0° to complete the

separation of the K picrate. This is filtered off and the filtrate is seeded with adenosine, which crystallises in 85% yield. H. W.

Synthesis in the alloxazine, isoalloxazine (flavin), and lumazine groups. III. **Synthesis of some acid derivatives.** K. GANAPATI (J. Indian Chem. Soc., 1938, 15, 121—128).—1:2:4- $C_6H_3(NH_2)_2 \cdot SO_3H$ and 1:2:4- $C_{10}H_5(NH_2)_2 \cdot SO_3H$ with alloxan yield *alloxazine-6- or -7-sulphonic acid* and 7:8-benzalloxazine-6-sulphonic acid or 5:6-benzalloxazine-7-sulphonic acid, respectively. No condensation takes place with β -naphthoquinone-4-sulphonic acid and uracil. β -o-Nitroanilinopropionic acid, obtained from o - $NO_2 \cdot C_6H_4 \cdot NH_2$ and $Br[CH]_2 \cdot CO_2H$, when reduced with $NaHSnO_2$ and condensed with alloxan in AcOH yields flavin-9-(β -)propionic acid and a substance, m.p. 219°. β -2-Nitro-4-methylanilinopropionic acid, m.p. 148—149°, obtained as above from 3:1:4- $NO_2 \cdot C_6H_3Me \cdot NH_2$, when reduced and condensed with alloxan gives no flavinpropionic acid, but a substance, m.p. 225°. 3:4-Diaminocinnamic acid with alloxan affords alloxazine-7- or -8-(β -)acrylic acid. A. L.

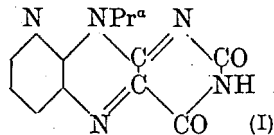
Mercury phthalocyanine.—See B., 1938, 765.

Determination of the m.p. of porphyrins and other darkly-coloured substances with the use of polarised light.—See A., 1938, I, 418.

Complex chemistry of iron in α -hæmins. A. F. RICHTER (Z. physiol. Chem., 1938, 253, 193—216).—In the addition to Fe of protohæmin, mols. with semipolar groups are favoured (e.g., aceto-, acetaldehyde-, aceto-, and, possibly, the cyanico-adduct). The tenacity of acetone in the acetohæmins depends on the nature of the polar component and the region of existence differs with the various compounds. The apparent impossibility of preparing alcohol- and ethero-adducts proves the importance of polar components in the orientation of the prosthetic group of the hypothetical protoporphyrin-iron [$C_{34}H_{32}O_4N_4Fe^+$]. The different orientation and polarity is designated as α -, β -, and meta-structure. In the case of the induced polarity of the alcoholic group, the binuclear complex, an ethanolodihæmin, must also be considered. The individuality of the β -modification appears to be established by the method of prep. and systematic crystallographical investigation. Küster's conception of the difference of the carboxyls in the symmetrical structure of the mol. finds no support and the representation that different demands are made on them by the free, non-coordinated basic N atoms contravenes the generally adopted constitutional formula of H. Fischer. It is therefore necessary to assume another course of the conjugated cyclus and explanation of the different polarity the existence of which and the consequent transformations are governed by the central Fe, since it has been shown that α - and β -protoporphyrin are only different modifications of the same substance. Further insight in this direction is obtained by the prep. of pure β -hæmins or metahæmins in alcohol in which the C_H influence is reduced to a min. and in which the betainising influence can be kept within bounds by the choice of added anions. Addition of I^-

leads to α -hæmin, of H_2PO_2' to metahæmin, and of Cl^- to β -hæmin. It must therefore be assumed that in alcoholic solutions of oxalato-hæmin the respective structures are in tautomeric equilibrium unless the chief rôle is to be assigned to the anion. H. W.

9-Propyl-8-azaflavin. H. RUDY and O. MAJER (Ber., 1938, 71, [B], 1243—1248).—2-Chloro-3-aminopyridine is converted by NH_2Pr^a , $CuSO_4$, and H_2O at 180° into 3-amino-2-propylaminopyridine, m.p. 58°, which readily condenses with alloxan in AcOH containing $ZnCl_2$ and H_3BO_3 to 9-propyl-8-azaflavin (I), decomp. 345—350° after darkening above 300° when rapidly heated. It shows all the typical flavin properties and resembles very closely the 9-alkyl-flavins (II). Its neutral solution is yellow with intense green fluorescence which is proper to the zwitterion since the salts with mineral acid or alkali are non-fluorescent. The absorption spectrum of (I) coincides very nearly with those of (II) or lacto-flavin. Irradiation of (I) with the unfiltered light of the Hg-vapour lamp decomposes (I); in daylight the fluorescence slowly disappears. The alkali salts of (I) are freely sol., whilst the Ag salt is orange-red and suitable for the separation of (I). Conc. HCl , HNO_3 , $Br-H_2O$, and $HCl + H_2O_2$ are almost without action. Dil. alkali causes rapid decomp. giving a compound with blue fluorescence. $Na_2S_2O_4$ decolorises and reduces (I) but the colour returns immediately on contact with air. The redox potential is distinctly negative and apparently not greatly different from that of the flavins. Reduction with Zn and HCl causes the appearance of a red radical as intermediate. Apparently replacement of the C_6H_5 nucleus by a C_5H_5N ring does not cause marked alteration of the flavin characteristics, at any rate as far as the 8-azaflavins are concerned. H. W.



Alkylloxymethylisooxazoles. C. MUSANTE (Gazzetta, 1938, 68, 240—246).— $OEt \cdot CH_2 \cdot CO \cdot CH_2 \cdot COMe$ and NH_2OH yield ($NaOEt-EtOH$) 5-methyl-3-ethoxymethylisooxazole, b.p. 90°/15 mm., oxidised ($AcOH-H_2O_2$) to 5-methylisooxazole-3-carboxylic acid (I). $OMe \cdot CH_2 \cdot C(NH) \cdot CH_2 \cdot COMe$ and NH_2OH give 5-methyl-3-methoxymethylisooxazole, b.p. 80—82°/15 mm., also oxidised to (I). E. W. W.

β -Nitrodicarboxylic esters and their transformation into oxidopyrrolidines. B. REICHERT and E. WEGNER (Ber., 1938, 71, [B], 1254—1259).—Condensation ($NaOEt-EtOH$) of $CH_2(CO_2Et)_2$ and $NO_2 \cdot CPh \cdot CHPh$ gives Et_2 β -nitro- $\alpha\beta$ -diphenylethyl-malonate, m.p. 132—133°. The following Et_2 -malonates are obtained similarly: β -nitro- β -phenyl- α -p-anisylethyl, m.p. 127°; β -nitro- β -phenyl- α -3:4-methylenedioxyphenylethyl, m.p. 136—138°. From the requisite substituted styrene the following Et_2 -malonates are prepared: β -nitro- α -o-methoxyphenylethyl, m.p. 53°; β -nitro- α -2:4-dimethoxyphenylethyl (I), m.p. 59°; β -nitro- α -o-hydroxyphenylethyl, m.p. 92°; β -nitro- α -3:4-methylenedioxyphenylethyl, m.p. 66°; (β -nitro- α -3:4-methylenedioxyphenylethyl)ethyl-, m.p.

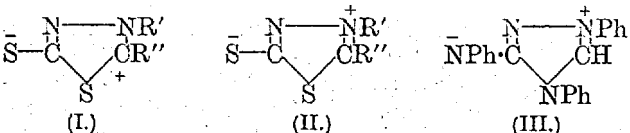
84—85°. Reduction (Pd-C in C_5H_5N) at about 50° of (I) leads to *Et* 1:2-oxido-2-hydroxy-4-2':4'-dimethoxyphenylpyrrolidine-3-carboxylate (cf. A), m.p. 145°, which appears incapable of reduction and does not appear to react with $SOCl_2$.

PCl_3 , $POCl_3$, or PCl_5 . *Et* 1:2-oxido-2-hydroxy-4-o'-methoxyphenylpyrrolidine-3-carboxylate, m.p. 106°, is hydrolysed by 10% HCl at 100° to the corresponding acid, m.p. 141° or (+1H₂O), m.p. 132—133° which at 160—170° gives CO_2 and 1:2-oxido-2-hydroxy-4-o'-methoxyphenylpyrrolidine, m.p. 139°. With Br in $CHCl_3$ it gives *Et* 3-bromo-1:2-oxido-2-hydroxy-4-o'-methoxyphenylpyrrolidine-3-carboxylate, m.p. 151°, and with NaOH and Me_2SO_4 it yields 1:2-oxido-2-methoxy-4-o'-methoxyphenylpyrrolidine-3-carboxylic acid, m.p. 144—145°. Phenanthrene-9-aldehyde, $MeNO_2$, and KOH in EtOH afford 9-β-nitrovinylphenanthrene, m.p. 173°.

Phenothiazine. III. Conversion of phenothiazine to thionol. F. DE EDS and C. W. EDDY (J. Amer. Chem. Soc., 1938, 60, 1446—1447).—The prep. of thionol (I) from phenothiazine and H_2O_2 -HCl-aq. EtOH is improved (80% yield). With boiling Ac_2O it gives the triacetate, m.p. 136.5°, and diacetate, m.p. 212°, of the leuco-base, which,

when pure, has an oxidation-reduction potential of 0.3019 v. at 21° and p_H 4.47. This potential is used as a criterion of purity.

Constitution and isomerism of certain triazole derivatives of the nitron type in the light of the Bredt rule and the theory of resonance. A. SCHÖNBERG (J.C.S., 1938, 824—825).—It is suggested that the endothiodihydrothiodiazoles are resonance hybrids of (I) and (II), that nitron is (III), and that,



in the endothio- and endooxy-triazolines, each of the classical formulæ must be replaced by two betaine formulæ, which explains the existence of isomerides.

F. R. S.

New heterocyclic syntheses. I. Triazoles and thiodiazoles. R. FUSCO and C. MUSANTE (Gazzetta, 1938, 68, 147—156).— $NHPh \cdot N : CPhCl$ (I) and 2:4:1- $C_6H_3Br_2 \cdot NH \cdot N : CPhBr$ (II) with $NH_2 \cdot CPh \cdot NH$ in cold Et_2O give 1:3:5-triphenyl- and 3:5-diphenyl-1-(2':4'-dibromophenyl)-1:2:4-triazole, m.p. 147°, respectively. With $KCNO$ in boiling 80% EtOH, (I) gives 1:3-diphenyl-1:2:4-triazol-5-one and (II) the *K* salt, m.p. 271°, of 3-phenyl-1-(2':4'-dibromophenyl)-1:2:4-triazole-5-one, m.p. 274°. With $CS(NH_2)_2$, 3:5-diphenyl-, m.p. 97° [hydrochloride, m.p. 247—248°; *Ac*, m.p. 157°, and *Bz*, m.p. 166°, derivatives; *NO*-derivative, m.p. 144° (decomp.)], which in xylene at 150° yields 2-keto-3:5-diphenyl-1:3:4-thiodiazoline, m.p. 85—86°, and 2-imino-5-

phenyl-3-(2':4'-dibromophenyl)-1:3:4-thiodiazoline, m.p. 98—100° [hydrochloride, m.p. 246°; *Ac*, m.p. 175—176°, and *Bz*, m.p. 198°, derivatives; *NO*-derivative, m.p. 144°, decomp. to 2-keto-5-phenyl-3-(2':4'-dibromophenyl)-1:3:4-thiodiazoline, m.p. 148—150°], are obtained. The same products are formed from $KSCN$.

E. W. W.

Acridine derivatives as antimalarials. II. V. P. BASU and S. J. DAS-GUPTA (J. Indian Chem. Soc., 1938, 15, 160—164).—2:5-Dichloro-7-methoxyacridine with 4-aminoantipyrene affords 2-chloro-7-methoxy-5-(1'-phenyl-2':3'-dimethyl-5'-pyrazolonylamino)acridine, m.p. 248°. In a similar way from the 5-chloroacridine and the aminoantipyrene or the thiazole derivative the following are obtained: 2-chloro-5-(1'-phenyl-2':3'-dimethyl-5'-pyrazolonylamino)-7-methylacridine, m.p. 257°, 3-nitro-5-(1'-phenyl-2':3'-dimethyl-5'-pyrazolonylamino)-7-methoxyacridine, m.p. 278—279°, 2:7-dichloro-5-(1'-phenyl-2':3'-dimethyl-5'-pyrazolonylamino)acridine, m.p. 276—277°, 2-chloro-5-(4'-phenylthiazolylamino)-7-methoxyacridine, m.p. 246—247°, 2-chloro-5-(4'-phenylthiazolylamino)-7-methylacridine, m.p. 263—264°, 2:7-dichloro-5-(4'-phenylthiazolylamino)acridine, m.p. 269—270°, 3-nitro-5-(4'-phenylthiazolylamino)-7-methoxyacridine, m.p. 264—265°, 2-chloro-5-(4'-methyl-5'-β-hydroxyethylthiazolylamino)-7-methoxyacridine, m.p. 256° (from 2-amino-4-methyl-5-β-hydroxyethylthiazole, m.p. 138°), 2-chloro-5-(4'-methyl-5'-β-hydroxyethylthiazolylamino)-7-methylacridine, m.p. 254°, 2:7-dichloro-5-(4'-methyl-5'-β-hydroxyethylthiazolylamino)acridine, m.p. 273°, 3-nitro-5-(4'-methyl-5'-β-hydroxyethylthiazolylamino)-7-methoxyacridine, m.p. 261—262°.

A. L.

Priority in the synthesis of vitamin-B₁. H. HÖRLEIN (Z. physiol. Chem., 1938, 253, 80—82).

W. McC.

Cactus alkaloids. XIX. N-Acetylmezcaline as component of mezcal buttons. E. SPÄTH and J. BRUCK (Ber., 1938, 71, [B], 1275—1276).—The isolation of N-acetylmezcaline [acet-β-3:4:5-trimethoxyphenylethylamide], m.p. 93—94°, from mezcal buttons is described.

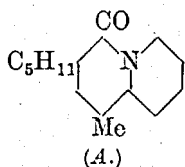
H. W.

Tobacco alkaloids. XV. Pictet's nicotine synthesis. E. SPÄTH and P. KAINRATH (Ber., 1938, 71, [B], 1276—1281).—An abbreviation and an emendation of Pictet's nicotine synthesis are described. 3-Aminopyridine (I) and mucic acid are distilled mainly at 250—300° and the 3'-pyridyl-1-pyrrole thus obtained, after removal of unchanged (I) by light petroleum, is isomerised to nornicotyrine (II) by passage through a tube packed with pumice at 700°. The crude product is separated by crystallisation into (II) and 3'-pyridyl-3-pyrrole (III), m.p. 140° [picrate, m.p. 198—199° (vac.; decomp.)], which gives nicotinic acid when oxidised. Catalytic hydrogenation (Pd sponge) of (II) gives nornicotine (dipicrate, m.p. 194°), methylated ($CH_2O \cdot HCO_2H$) to *dl*-nicotine. Hydrogenation of (III) affords 3-pyridyltetrahydropyrrole [dipicrate, m.p. 239° (vac.; decomp.)], methylated to 3'-pyridyl-1-methyltetrahydropyrrole (dipicrate, m.p. 193—195°).

H. W.

Sparteine. Hofmann degradation of oxysparteine. E. SPÄTH and F. GALINOVSKY (Ber., 1938,

71, [B], 1282—1287.—Oxysparteine is converted by MeI in MeOH at 100° into the *methiodide*, m.p. 223—225° (vac.), converted by Ag₂O followed by distillation into *de-N-methyloxysparteine* (I), m.p. 89—90°, $[\alpha]_D^{18}$ —17.13° in MeOH (mutarotation), $[\alpha]_D^{18}$ +4.82° (const.) in C₆H₆. This is reduced (PtO₂ in HCl) to *de-N-methyldihydro-oxysparteine* (*picrate*, m.p. indef. 129—132°), which affords an amorphous *methiodide* which does not give satisfactory results when the Hofmann degradation is attempted. (I) is therefore converted into the amorphous methiodide and thence into *de-N-dimethyloxysparteine* (*perchlorate*, m.p. 209—210°; *picrate*, m.p. 135—136°, $[\alpha]_D^{18}$ —0.63° in MeOH), which yields the optically inactive *de-N-dimethyltetrahydro-oxysparteine*. The corresponding *methiodide*, m.p. 185—187° (vac.; indef.), is converted through the hydroxide into *tetrahydrohemioxysparteylene*, whence *hexahydrohemioxysparteylene* (A), b.p. 130—140° (bath)/0.01 mm., which is optically inactive and does not yield cryst. salts or derivatives.



Absorption of the chief cinchona alkaloids in the ultra-violet. L. FUCHS and A. KAMPITSCH (Sci. pharm., 1935, 6, 113—122; Chem. Zentr., 1936, ii, 818).—Ultra-violet absorption spectra in H₂O and EtOH of quinine, cinchonidine, cinchonine, quinidine, of their neutral salts (spectrum type I), and of their acid salts (type II) are determined. The first pair under comparable conditions show almost identical spectra as do also the second pair, but the chromophoric OMe differentiates the quinine from the cinchonine spectrum. Minor solvent effects are also noted.

H. W.
A. H. C.

So-called 2-nitrosomorphine. E. OCHIAI and T. NAKAMURA (Proc. Imp. Acad., Tokyo, 1938, 14, 134—136).—The 2-nitrosomorphine of Wieland *et al.* (A., 1911, i, 743) is shown to be 2-nitromorphine by analysis of its forms, anhyd. and +H₂O, and of its hydrochloride, anhyd. and +2.5H₂O, by hydrogenation (3 H₂ absorbed) in dil. HCl in presence of Pd-C to non-phenolic 2-aminodihydromorphine (*dihydrochloride*, decomp. 325°; B₂ derivative, m.p. 185°), by absence of a Liebermann reaction, and indifference to HI.

R. S. C.

Oxidation of mesaconitine, aconitine, and their oxidation product, oxonitine. H. SUGINOME (J. Fac. Sci. Hokkaido Univ., III, 1937, 2, 95—114).—Details are given of results already reviewed (A., 1938, II, 74). Triacetyloxonitine contains xH₂O of crystallisation. Nitronitrosoaconitinic acid crystallises from aq. COMe₂ with H₂O and 0.5 or 1H₂O. Ba nitronitrosoaconitinate contains 8H₂O. AcCl introduces 2 Ac into nitronitrosoaconitine acid, one replacing the NO, which (not the NO₂; cf. *loc. cit.*) is attached to N. Aconitine (I) is C₁₈H₁₇(OMe)₄(OH)₃(OAc)(OBz)(NEt·CH₂); mesaconitine (II) is C₁₈H₁₇(OMe)₄(OH)₃(OAc)(OBz)(NMe·CH₂). Oxonitine is prepared from (II) in 79% yield by KMnO₄ (4 O), but only in 30% yield from (I) (best with 6 O).

R. S. C.

Hydrocyanic acid compounds of alkaloids and organic bases. P. MESNARD (Bull. Trav.

Soc. Pharm. Bordeaux, 1936, 74, 35—56; Chem. Zentr., 1936, ii, 1732).—The compounds are prepared by slowly crystallising (nicotine and atropine compounds are not cryst.) a solution of a salt of the base with a neutralised (H₂SO₄) mixture of equal vols. of 5% CuSO₄·5H₂O and 6% KCN solutions. The base in these compounds is determined by pptg. with NaOH, extracting, and weighing or titrating. The compounds are of three types: xCuCN, y(B,HCN); xCuCN, y(B,HCN), zHCN; xCuCN, y(B,HCN), zB (B = base). Derivatives of the following bases are described: cocaine, CuCN, 4(C₁₇H₂₁O₄N,HCN), 4HCN; novocaine, CuCN, (C₁₃H₂₀O₂N₂,HCN), HCN; p-amino-benzoyldibutylaminoethanol, CuCN, 2(C₁₈H₃₀O₂N₂,HCN), HCN; benzoyldiethylaminodimethylethylcarbinol,

3CuCN, 4(C₁₆H₂₅O₂N,HCN), HCN; morphine, CuCN, 9(C₁₇H₁₉O₃N,HCN), 7HCN; codeine, CuCN, 4(C₁₈H₂₁O₃N,HCN), 3HCN; ethylmorphine, CuCN, 5(C₁₉H₂₃O₃N,HCN), 2HCN; benzoylmorphine, CuCN, 4(C₂₄H₂₅O₃N,HCN), HCN; diacetylmorphine, CuCN, 5(C₂₁H₂₃O₃N,HCN), 2HCN; NHPh·NH₂, 3CuCN, 4(C₈H₉N₂,HCN), HCN; sparteine, 3CuCN, 2(C₁₅H₂₆N₂, 2HCN); quinine, CuCN, 4(C₂₀H₂₄O₂N₂,HCN); cinchonidine, CuCN, 8(C₁₉H₂₂ON₂,HCN); strychnine, CuCN, 2(C₂₁H₂₆O₂N₂,HCN); brucine, 2CuCN, 5(C₂₂H₂₆O₄N₂,HCN); piperidine, CuCN, 5(C₅H₁₁N,HCN); methylene-blue, 2CuCN, 13(C₁₆H₁₈N₃SO₃,HCN), 5HCN; nicotine, CuCN, 2(C₁₀H₁₄N₂,HCN), 1.5HCN; atropine, 2CuCN, 3(C₁₇H₂₃O₃N,HCN), 3HCN; hordenine, CuCN, (C₁₀H₁₅ON,HCN), HCN; l-ephedrine, CuCN, 6(C₁₀H₁₅ON,HCN), 5HCN; caffeine, 4CuCN, (C₈H₁₀O₂N₄,HCN); CuCN, 9(NH₂Ph,HCN); pyrimidone, CuCN, 4(C₁₃H₁₁ON₃,HCN), 3HCN; 4CuCN, 3(C₅H₅N,HCN), 9HCN; CuCN, 5[(CH₂)₆N₄,HCN]; antipyrine, 6CuCN, (C₁₁H₁₂ON₂,HCN), 12C₁₁H₁₂ON₂; quinoline, 5CuCN, (C₉H₇N,HCN), 4C₉H₇N.

A. H. C.

Cinchona alkaloids in pneumonia. VI. Hydroxyalkylation of phenolic cinchona alkaloids. C. L. BUTLER and (MISS) A. G. RENFREW (J. Amer. Chem. Soc., 1938, 60, 1473—1475; cf. A., 1937, II, 171).—p-C₆H₄Me·SO₃·[CH₂]₂·O·CH₂Ph, apocupreine, and KOH-EtOH at 100° give β-benzoyloxyethylapocupreine (I), m.p. 115°, $[\alpha]_D$ —155°, obtained also from the β-chloroethyl ether (*dihydrochloride*, $[\alpha]_D$ —205°). The product is stable to NaOH, but is hydrolysed by 11% HCl to β-hydroxyethylapocupreine (II) (*dihydrochloride*, $[\alpha]_D$ —228°; Ac₂ derivative, amorphous). Isolation of (I) is unnecessary for the prep. of (II), and β-hydroxyethylcupreine, $[\alpha]_D$ —131° (*dihydrochloride*, $[\alpha]_D$ —181°; amorphous Ac₂ derivative, $[\alpha]_D$ —30°), γ-hydroxypropyl-, m.p. 140°, $[\alpha]_D$ —181° (*dihydrochloride*, $[\alpha]_D$ —225°; Ac₂ derivative, $[\alpha]_D$ —69°), β-hydroxyisopropyl- (III), m.p. 105—108°, $[\alpha]_D$ —180° (*dihydrochloride*, $[\alpha]_D$ —224°; Ac₂ derivative, a gum, $[\alpha]_D$ —61°), and ββ'-dihydroxyisopropyl-apocupreine, m.p. 128°, $[\alpha]_D$ —177° (*dihydrochloride*, $[\alpha]_D$ —203°; Ac₃ derivative, amorphous, $[\alpha]_D$ —46°), are thus prepared. These OH-ethers, especially (III), have high toxicity to pneumococci *in vitro*, but cause little eye-damage to dogs. $[\alpha]$ are in EtOH. R. S. C.

Arsenated derivatives of mixed ketones. II. **Arsenicals of pæonol.** C. K. BANKS and C. S. HAMILTON (J. Amer. Chem. Soc., 1938, 60, 1370—1371; cf. A., 1937, II, 267).—5-Nitro-2-hydroxy-4-methoxyacetophenone [prep. in 80% yield by HNO_3 (d 1.42) at 15–10°, m.p. 155°, is reduced quantitatively by H_2 -Raney Ni in COMe_2 (only with difficulty by H_2 -PtO₂) to the unstable 5- NH_2 -compound, m.p. 115° (hydrochloride, m.p. 250°), which by a diazo-reaction affords 2-hydroxy-4-methoxyacetophenone-5-arsinic acid, m.p. 225° (decomp.). HCl - NaI - SO_2 then affords the arsenious oxide, m.p. 260° (decomp.), reduced by HPO_2 to 4:4'-dihydroxy-5:5'-diacetyl-2:2'-dimethoxyarsenobenzene, m.p. 228° (decomp.).

R. S. C.

Antimony compounds of 8-hydroxyquinoline. M. DENAYER (Cong. Chim. ind. Bruxelles, 1935, 15, I, 387—391; Chem. Zentr., 1936, ii, 1926).—Whilst Sb_2O_3 yields with Na 8-hydroxyquinoline-5-sulphonate the ester $(\text{C}_9\text{H}_5\text{O}_4\text{NSNa})_3\text{Sb}$, which is hydrolysed by alkali, Na 7:8-dihydroxy- and 7-amino-8-hydroxy- (but not 7-acetamido-8-hydroxy-)quinoline-5-sulphonates yield alkali-stable compounds. Compounds of Sb^{V} are also described.

A. H. C.

Phenylmercuric compounds. J. K. GJALDBÆK and V. H. MIKKELSEN (Arch. Pharm. Chem., 1938, 11, 1—100).—A complete crit. review of the literature on the prep., properties, qual. and quant. analysis, and pharmacological applications of HgPh salts. Many consts. have been determined and errors corr. HgPh salts when warmed with aq. KI_3 give PhI . HgPh salts insol. in H_2O are determined by dissolution in excess of 0.1N- NaOH in COMe_2 - EtOH and back-titration. Their reactions with Cu , Zn , Sn , Na_2S , $(\text{NH}_4)_2\text{S}_x$, and $\text{Na}_2\text{S}_2\text{O}_3$ have been investigated. The dissociation and hydrolysis of $\text{HgPh}\cdot\text{OH}$ and $\text{HgPh}\cdot\text{OAc}$ in aq. solution have been studied. Hg^{II} Ph thiosulphate, m.p. >270°, and metaborate, m.p. 185—190°, and $\text{HgPh}\cdot\text{BO}_2$, $\text{HgPh}\cdot\text{OH}$, m.p. 120°, have been prepared.

M. H. M. A.

Introduction of the MgBr group into anisole and phenetole. F. CHALLENGER and S. A. MILLER (J.C.S., 1938, 894—899).—2-Thienylmagnesium bromide, S , and PhOEt (I) give a product, which on reduction (Zn - HCl) and treatment with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ affords phenethylthiolacetic acid, m.p. 64—65°. MgEtBr and (I), followed by HgBr_2 , yield *o*-phenethylmercury bromide, converted into di-*o*-phenethylmercury. PhOMe with MgEtBr or MgPr^nBr similarly gives *o*-anisylmercury bromide: no *p*-compounds are formed. (I) does not react appreciably with S at its b.p., nor is (I) or PhOMe mercurated by HgCl_2 or HgBr_2 . *o*-Anisidine, HgBr_2 , HBr , and NaNO_2 give *o*-anisyl-diazonium-mercury tribromide, m.p. 117—118°, which with Cu affords *o*-anisylmercury bromide; the corresponding *p*-diazonium compound, m.p. 138—139°, similarly yields *p*-anisylmercury bromide, also obtained from p - $\text{C}_6\text{H}_4\text{Br}\cdot\text{OMe}$. NPhMe_2 , MgEtBr , and CO_2 give dimethylantranilic acid.

F. R. S.

Reactivity of the double linking in coumarins and related $\alpha\beta$ -unsaturated carbonyl compounds. VI. Action of mercuric acetate on the methyl ethers of coumarinic and coumaric acids. S. RANGASWAMI, V. S. RAO, and T. R. SESHADRI (Proc.

Indian Acad. Sci., 1938, 7, A, 312—318; cf. A., 1938, II, 300).—The Me ether (I) of coumarinic acid with $\text{Hg}(\text{OAc})_2$ in MeOH at 28° gives α -acetoxymercuri- β :2-dimethoxy- β -phenylpropionic acid, decomp. 204°, which loses AcOH giving an anhydride (Billmann, A., 1912, i, 461) when a solution in aq. NaOH is acidified with dil. H_2SO_4 ; with dil. HCl removal of the addenda occurs with the formation of the isomeric Me ether of coumaric acid. When heated with >3 mols. of $\text{Hg}(\text{OAc})_2$ in MeOH (20 hr.) (I) gives α :3:5-triacetoxymercuri- β :2-dimethoxy- β -phenylpropionic acid, decomp. 220—221°; an alkaline solution with HCl gives 3:5-dichloromercuri-2-methoxycinnamic acid, decomp. 216°, whereas with H_2SO_4 a sulphatomercuric compound, $\text{C}_{11}\text{H}_{10}\text{O}_8\text{SHg}_3$, decomp. 226°, is obtained. The foregoing mercuric compounds with H_2S in alkaline solutions give β :2-dimethoxy- β -phenylpropionic acid (cf. loc. cit.). The Me ether of coumaric acid when treated with $\text{Hg}(\text{OAc})_2$ in MeOH in the cold gives an indefinite, partly mercurated additive product, but with >3 mols. of $\text{Hg}(\text{OAc})_2$ in boiling MeOH (20 hr.) the compounds obtained are identical with those from (I). By similar methods the Me ether (II) of 5-nitrocoumarinic acid first gives its Hg salt, decomp. 141—142°, which slowly changes into α -acetoxymercuri-5-nitro- β :2-dimethoxycinnamic acid (III), decomp. 199°, converted (H_2SO_4 on alkaline solution) into the anhydride form (IV), decomp. 210°, also obtained from (II) and $\text{Hg}(\text{OAc})_2$ in MeOH (100°; 5 hr.). Acidification of a solution of (III) or (IV) in aq. NaOH with HCl gives the Me ether of 5-nitrocoumaric acid. This with $\text{Hg}(\text{OAc})_2$ gives its Hg salt, decomp. 205°, which changes slowly into (III). Alkaline solutions of (III) and (IV) with H_2S give 5-nitro- β :2-dimethoxy- β -phenylpropionic acid, m.p. 158°. The NO_2 -acids undergo addition only; elimination of the addenda by dil. HCl gives the *trans*-form in each case.

H. G. M.

Decomposition reactions of aromatic diazo-compounds. IV. New synthesis of aromatic antimony compounds. F. B. MAKIN and W. A. WATERS (J.C.S., 1938, 843—848; cf. A., 1938, II, 52).—Solid p - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\text{Cl}$ and p - $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{Cl}$ with COMe_2 at 50°, with or without CaCO_3 , yield PhCl and PhBr , respectively, and $\text{CH}_2\text{Cl}\cdot\text{COMe}$, whilst with Hg and CaCO_3 in COMe_2 , p - $\text{C}_6\text{H}_4\text{Hal}\cdot\text{HgCl}$ are obtained. In EtOAc with CaCO_3 at 60°, p - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\text{Cl}$ yields p - $\text{C}_6\text{H}_4\text{Cl}_2$, but no PhCl ; it is decomposed in the cold by Pb , Ag , or Bi , in COMe_2 or EtOAc . Decomp. of ArN_2Cl by Sb in presence of CaCO_3 , in COMe_2 or AcOEt (but not in H_2O , EtOH , cyclohexane, C_6H_6 , CCl_4 , CS_2 , Et_2O , or dioxan), yields mixtures of SbAr_3Cl_2 , SbAr_3 , and SbAr_2Cl ; it is inferred that reaction occurs only after tautomeric change to the wholly covalent $\text{NAr}\cdot\text{NCl}$. ArN_2Cl , SbCl_3 and ArN_2Cl , ZnCl_2 give similar results in COMe_2 . In this way the following compounds have been prepared: *tri-p-chloro-* (in COMe_2), m.p. 193°, and (in COMe_2 or EtOAc) *p-bromo-phenyl-*, m.p. 200°, *tri-(4- (from ZnCl_2 double salt in COMe_2), m.p. 264°, and (in EtOAc) -5-chloro-*o*-tolyl)-*, m.p. 238°, and (in EtOAc) *tri-(5-chloro-2-methoxyphenyl)-stibine dichloride*, m.p. 281° (decomp.) (the last three also obtained from the stibine and Cl_2 in CCl_4); *tri-(4-, m.p. 226°, and -5-chloro-*o*-tolyl)-*, m.p. 176° (both in COMe_2 or EtOAc),

and (in EtOAc) *tri*-(5-chloro-2-methoxyphenyl)-stibine, m.p. 188°; *di*-(5-chloro-2-methoxyphenyl)- (in COMe₂), m.p. 144°, and (from the ZnCl₂ double salt in COMe₂) *di*-(4-chloro-*o*-tolyl)-stibinous chloride, m.p. 131°. The last with Cl₂ in CCl₄ gives the *stibinic trichloride*, m.p. 162°.

A. Li.

Di-indolepalladium hydrochloride. L. DELAVIGNE (Gazzetta, 1938, 68, 271—272; cf. A., 1938, II, 29).—PdCl₂ and indole in H₂O give the compound, C₁₆H₁₄N₂Cl₂Pd (? *di*-2-indolylpalladium + 2HCl).

E. W. W.

Organometallic compounds. F. HEIN (Angew. Chem., 1938, 51, 503—508).—A lecture reviewing recent work.

Structure of proteins (wool, fibroin, gelatin). D. KRÜGER (Chem.-Ztg., 1938, 62, 533—535).—A review.

Copper tube preheater [for micro-analyses of carbon and hydrogen]. W. MACNEVIN and H. S. CLARK (Ind. Eng. Chem. [Anal.], 1938, 10, 338).—The preheater consists of Cu tubing wound for a part of its length into the form of a coil which is heated by means of a batwing burner. Air saturated with colloidal oil and other org. impurities gave a negligible blank when this heater was used.

L. S. T.

Nitrogen determinations by the micro-Dumas method.—See A., 1938, I, 414.

Determination of active hydrogen in organic compounds. E. J. SHTUBER and A. V. DOBROMISLOVA (J. Appl. Chem. Russ., 1938, 11, 704—706).—Labile H is determined by a modified Tschugaev-Zerevitinov method, involving exclusion of atm. O₂, and replacement of *iso*-C₅H₁₁·OH by xylene.

R. T.

Colorimetric determination of small amounts of chloropicrin in air, water, and foodstuffs. W. DECKERT and B. PRATHITHAYANJA (Z. anal. Chem., 1938, 113, 182—189).—The yellow colour formed by CCl₃·NO₂ (I) and NPhMe₂ (50% in C₆H₆ solution) in presence of O₂ (H₂O₂) forms the basis of the colorimetric determination of 10 to 5000 µg. of (I) in air, H₂O, and foodstuffs. (I) is extracted from H₂O by shaking with a 50% solution of NPhMe₂ in C₆H₆, and from dry foodstuffs such as bread, potatoes, flour, and corn by extraction with C₆H₆. Distillation with xylene is used for separating (I) from fatty substances, and distillation in xylene vapour for separation from milk etc. The application of the reaction to the detection of traces of (I) in air using the Dräger-Schröter apparatus is also described.

L. S. T.

Determination of glycerol and some other hydroxyl compounds. S. H. BERTRAM and R. RUTGERS (Rec. trav. chim., 1938, 57, 681—687).—Glycerol (I) is determined by means of the Cu Na compound, +1.5H₂O, which is sol. in aq. EtOH. CuCl₂·EtOH is added to (I) and NaOH in aq. EtOH until a ppt. is just formed, the mixture centrifuged, and the Cu in the supernatant liquor determined by Na₂S₂O₃. The technique needed for determining the (I) liberated by hydrolysis of oils and fats is also detailed. Slight variation in temp., concn. of NaOH or EtOH, or time of keeping does not vitiate the result. The

(I) content may be 0—0.9 g. per 10 c.c. A blank determination is necessary. Three technical samples of (I) were 84, 91.65, and 86.5% pure. Glucose, sucrose, lactose, etc. and CH₂(CH₂·OH)₂ do not interfere. Mannitol and sorbitol (2 Cu per mol.), and (OH·CH·CO₂H)₂ (1 Cu per mol.) are similarly determined.

R. S. C.

Manganese as catalyst and redox indicator in the cerimetric determination of oxalate. L. SZEPELLÉDY and S. TANAY (Pharm. Zentr., 1938, 79, 441—447).—Mn⁺⁺ ions catalyse the reaction between C₂O₄^{''} and Ce⁺⁺⁺⁺. The solution containing C₂O₄^{''} is mixed with 10 c.c. of 5N-H₂SO₄ or 5 c.c. of conc. HCl, and diluted to 50 c.c. 1 g. of MnSO₄·5H₂O or MnCl₂·4H₂O and 0.05 c.c. of ferroin indicator solution (1.624 g. of *o*-phenanthroline hydrochloride and 0.695 g. of FeSO₄·7H₂O in 100 c.c. of H₂O) are added, and the solution is titrated (pale blue) with 0.1N-Ce(SO₄)₂ solution. The results agree with those obtained potentiometrically, by titration with Ce(SO₄)₂ using ICl as catalyst, and by direct titration with KMnO₄. The Mn salt can also serve as a redox indicator, and, in daylight, the use of ferroin is unnecessary. For micro-determinations, the C₂O₄^{''} solution is mixed with 1 c.c. of 5N-H₂SO₄ (or HCl) and 0.10 g. of MnSO₄·5H₂O (or MnCl₂·4H₂O), 0.01 c.c. of ferroin solution, which is indispensable in this case, diluted to 5 c.c., and titrated with 0.1N-Ce(SO₄)₂ solution at 40—50°.

L. S. T.

Polarographic analysis of mixtures of *cis*- and *trans*-aconitic acids. G. SEMERANO and L. SARTORI (Mikrochem., 1938, 24, 130—133).—These acids can be detected and determined as their Ca salts in a solution of NH₄Cl. The reduction potentials of the acids are sufficiently different; the strength of the diffusion current ∝ concn. Since at a given concn. the current with the *cis*-salt is somewhat > that with the *trans*-compound, the detection of the *cis*-acid in presence of much *trans*-acid is easier than the reverse. The Li salts serve for the detection of the *trans*- in presence of the *cis*-acid but not vice versa.

L. S. T.

Organic acid-ferrous complex as a disturbing factor in the titrimetric determination of ascorbic acid. K. P. BASU and M. C. NATH (J. Indian Chem. Soc., 1938, 15, 133—135).—Organic acid-Fe^{II} complexes exert a powerful reducing action on 2:6-dichlorophenol-indophenol used in the determination of ascorbic acid. The reducing power has been determined for oxalic, malonic, succinic, malic, tartaric, and citric acids; neither Fe⁺⁺ nor the acid alone reduces the reagent. For the dibasic acids the reducing power of the complex decreases as the no. of C atoms in the acid increases. The citric acid-Fe^{II} complex is incompletely removed by Hg(OAc)₂.

E. S. H.

Thioketonic esters. VII. Thio-thiol estimation. S. K. MITRA (J. Indian Chem. Soc., 1938, 15, 205—210).—Determination of thiol in CSMe·CH₂·CO₂Et, CSMe·CHMe·CO₂Et, CSMe·CHBu^β·CO₂Et, and CSMe·CH(CO₂Et)₂ by adding the ester to an excess of EtOH-I at -7° and titrating with Na₂S₂O₃ shows that α-substitution increases the percentage of the SH form.

A. Li.

Use of glycerol instead of Seignette salt in determination of sugars by Bertrand's method. M. N. TULTSCHINSKI (J. Appl. Chem. Russ., 1938, 11, 707—710).—5 ml. of 21.2% glycerol, 15 ml. of 20% KOH, and 20 ml. of 4% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are added to 20 ml. of solution, and determination of sugar is conducted further according to Bertrand. The results deviate from those given by the original method, to an extent cc sugar content, and require the application of an empirical correction. R. T.

Determination of choline and acetylcholine.—See A., 1938, III, 706.

Determination of amino-acids. T. LAINE (Suomen Kem., 1938, 11, A, 50—52, 65—67).—A review of methods. The determination of naturally occurring NH_2 -acids is discussed in detail.

M. H. M. A.

Derivatives of the indane group as reagents for amines. I. Detection of primary monoamines with bindone. G. WANAG (Z. anal. Chem., 1938, 113, 21—34).—Primary aromatic amines yield with bindone in glacial AcOH a blue colour which furnishes a delicate test for traces of such amines. A similar colour is given with monoalkylarylamines, but the test is much less sensitive. Primary aliphatic and alicyclic amines yield a violet colour, whilst sec. aliphatic amines give this colour only in very conc. solution. Di- and tri-aryl-, diarylalkyl-, and trialkyl-amines, $\text{C}_5\text{H}_7\text{N}$, quinoline, pyrrole, and alkaloids give no characteristic colour. J. W. S.

Identification of sulphanilamide. J. V. SCUDRI (Ind. Eng. Chem. [Anal.], 1938, 10, 346—347).—A solution of sulphanilamide (I) (1 drop containing 0.04 mg.) with 40% CH_2O (1 drop) and 10% Na_2CO_3 (1 drop) affords a *polymeride*, $(\text{C}_6\text{H}_8\text{O}_2\text{N}_2\text{S})_x$, m.p. 235—240° (decomp.); 0.012 mg. of (I) can be detected microscopically. (I) (1 drop containing 0.02—0.04 mg.) with ICl (1 drop) affords 3:5-di-iodo-4-amino-benzenesulphonamide (cf. A., 1937, II, 409). (I) (as hydrochloride) affords a *picrate*, m.p. 179—180°; 0.012 mg. can be detected microscopically. (I) (1 drop containing 0.04 mg.) with $\text{Hg}(\text{NO}_3)_2$ (1 drop) and 10% Na_2CO_3 (1 drop) affords a flocculent ppt. best seen with dark background illumination. Equimol. amounts of (I) and AgNO_3 in the presence of aq. NH_3 afford a white *compound*, $\text{C}_6\text{H}_7\text{O}_2\text{N}_2\text{S} \cdot \text{Ag}$, but the test is insensitive. With $(\text{NH}_4)_2\text{S}_2\text{O}_8$, (I) affords evanescent colours. (I) when boiled with conc. HNO_3 and then made alkaline with NaOH affords an intense yellow colour with concns. >10%. A few mg. of (I) with cold Ac_2O afford acetylsulphanilamide (cf. *loc. cit.*) but with boiling Ac_2O , *diacetylsulphanilamide*, m.p. 242—244° (decomp.), is formed. *s-Diphenylcarbamide-4:4'-disulphonamide* has m.p. 270—271° (decomp.). J. L. D.

Optical crystallographic studies with the polarising microscope. I. Identification and semi-quantitative determination of acetic and propionic *p*-bromoanilides in their binary mixtures. W. M. D. BRYANT (J. Amer. Chem. Soc., 1938, 60, 1394—1399).—The optical crystallographic consts. of three forms of acet-*p*-bromoanilide (I) and of two forms of propion-*p*-bromoanilide (II) have been determined. The acute and obtuse optic axial angles in

cedar oil have also been measured. Optic axial angles of mixed crystals of (I) and (II) have been determined for five monochromatic radiations of the Hg arc. M.p. of mixtures of (I) and (II) of different composition have been determined; the system apparently fails to form a eutectic. The above data serve as the basis of a method for the identification of small amounts of AcOH and EtCO_2H and for determining roughly the composition of their mixtures. The mixed crystal system of (I) and (II) shows three types of crystal dispersion: axial, crossed axial plane, and monoclinic crossed dispersion. The first and second are functions of composition. E. S. H.

Detection and determination of ouabain and strophanthin. W. D. RAYMOND (Analyst, 1938, 63, 478—482).—The colour given by ouabain (I) with conc. H_2SO_4 and Ac_2O cannot be used to evaluate the drug quantitatively. (I) with naphthoresorcinol—conc. HCl at 50° affords a pink colour after 10 min. [strophanthin-*k* (II) and -*e* similarly afford green and red colours, respectively]; an amyl-alcoholic extract of the diluted solution shows a green fluorescence with >0.004 mg. of (I), but not with (II). (I) with COMe_2 —conc. HCl at 100°, followed by extraction with CHCl_3 , affords a pink colour. (II) does not give the reaction. (I) or (II) with *m*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$ or *o*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ (III) in EtOH at 0° followed by treatment with 20% NaOH gives an indigo-blue or violet colour with the former reagent and a red with the latter. With (III) the colour is sufficiently stable to allow quant. measurements. (I) or (II) in boiling AcOH containing furfuraldehyde and ZnCl_2 affords a blue colour. Anhyd. (I) with $\text{ZnCl}_2 \cdot \text{Ac}_2\text{O}$ at 70° affords *hepta-acetyl-anhydro-ouabain*, m.p. 283—284°. J. L. D.

Microchemistry of methylxanthines (caffeine, theobromine, theophylline). G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1936, 74, 5—11; Chem. Zentr., 1936, ii, 505).—A reaction of the hydrochlorides with NaBr—NaOBr is described.

H. N. R.

Volumetric determination of diethyl- or diallyl-barbituric acid. Determination of barbituric acid derivatives in presence of acetic, salicylic, and phenylcinchonic acids, theobromine, and theophylline. E. SCHULEK and P. RÓZSA (Z. anal. Chem., 1938, 112, 404—415).—A wt. of substance corresponding with 0.1 to 0.15 g. of diethyl- or diallyl-barbituric acid is dissolved in 5% borax solution, K_2CrO_4 solution is added as indicator, and the hot solution titrated with 0.1N- AgNO_3 . The method is not suitable for phenylethylbarbituric acid and other barbiturates. For the separation of these derivatives from various org. acids and from theobromine the procedure described utilises the fact that the alkali barbiturates are decomposed by H_2CO_3 to give the cryst. acids sol. in Et_2O . A method for the determination of diethylbarbituric acid in urine in presence of salicylic acid is also described.

L. S. T.

Determination of flavin.—See A., III, 676.

Separation and determination of phytin.—See A., III, 706.

Microchemical determination of chlorophyll and of cuprophyll.—See A., 1938, III, 706.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

SEPTEMBER, 1938.

Structural definition of auxochromes and chromophores. M. ARTINET (Bull. Soc. chim., 1938, [v], 5, 1033—1042).—The at. groups causative of coloration or selective absorption can be divided into auxochromes and chromophores and this distinction appears advisable. To each of these groups can be given a definition based on the consideration of their structure and from which it can be predicted that the accumulation in a single mol. solely of chromophores or solely of auxochromes is much less favourable to the development of colour than the simultaneous presence of members of each of the two groups.

H. W.

Deuterium and optical activity. C. BUCHANAN (Chem. and Ind., 1938, 748—751).—A review.

A. LI.

Kinetics of the thermal decomposition of *n*-butane.—See A., 1938, I, 403.

Synthesis of *n*-heptane. V. V. TISCHTSCHENKO and M. A. BELOPOLSKI (J. Appl. Chem. Russ., 1938, 11, 638—642).—BuOH is oxidised to PrCHO, and this to PrCO₂H, by known catalytic methods. PrCO₂H is passed over ThO₂ gel at 400° to give COPr₂, which is hydrogenated (MoS₃ catalyst, at 350°/100—110 atm.) to yield *n*-heptane, by the reactions: COPr₂ → CHPr₂·OH → CHEt·CHPr → *n*-C₇H₁₆.

R. T.

Peroxide effect in the addition of reagents to unsaturated compounds. XV. Correction. F. R. MAYO (J. Org. Chem., 1938, 2, 577; cf. A., 1938, II, 122).

R. S. C.

Influence of substituents on the spontaneous or thermal polymerisation of olefines. F. EIRICH (Österr. Chem. Ztg., 1938, 41, 251—254).—A lecture.

E. S. H.

Mercury-photosensitised hydrogenation of ethylene, tetradeuteroethylene, and partly deuterated ethylenes.—See A., 1938, I, 408.

Explosive decomposition of acetylene with ignition. A. GROSS (Compt. rend., 1938, 206, 1654—1656; cf. A., 1928, 28).—C₂H₂, pure or diluted with an inert gas, when passed through certain tubes (listed) of various diameters and at different temp. does not ignite. Using other tubes (e.g., Pyrex, SiO₂, Fe, graphite), white fumes changing to yellow and then to brown issue from the tube, and there is periodic ignition of the gas, and a deposit of C. The temp. at which the phenomenon occurs varies from 550—600° and 850—900° depending on the tube. The period of ignition varies with the temp. and rate of flow of C₂H₂ and is independent of the dilution of C₂H₂. The phenomenon is probably due to two

reactions, polymerisation and decomp. of C₂H₂, and is catalysed by the material of the tube. The reaction is not a chain reaction because the presence of inert gas is without effect.

J. L. D.

Fluorination method. A. L. HENNE (J. Amer. Chem. Soc., 1938, 60, 1569—1571).—Passing HF into a stirred mixture of red HgO and an org. substance leads to smooth replacement of Cl or Br in the org. substance by F, if efficient cooling is provided. Yields, usually > 70%, are often improved by cooling, e.g., to —20°. Indifferent solvents may be used. Complete exchange occurs with CH₂Cl₂, CH₃Br·CH₃·OAc, CHBr₂·CH₂·OAc, CHMeCl₂, *n*-C₆H₁₃·CHCl₂, CPh₂Cl₂, and CPh₃Cl. CHCl₃ gives CHClF₂. (CCl₃F)₂ gives (CClF₂)₂. CHCl₂·CClF₂ or CHF₂·CCl₃ gives CHF₂·CClF₂. A quant. method of recovering the Hg is described.

R. S. C.

Photochemical polymerisation of chloroprene and related molecules.—See A., 1938, I, 408.

Peroxide effect in the addition of reagents to unsaturated compounds. XVII. Addition of hydrogen sulphite. M. S. KHARASCH, E. M. MAY, and F. R. MAYO (Chem. and Ind., 1938, 774—775).—O₂ and peroxides catalyse the addition of NaHSO₃ to allyl alcohol, styrene, and CHPh·CH·CH₂·OH; in their absence very little action occurs. A chain mechanism is proposed.

H. W.

Scission of primary and secondary β-ethylenic alcohols. C. PRÉVOST and O. K. HOVO (Compt. rend., 1938, 206, 1661—1662; cf. A., 1928, 1211).—Alcohols R·CH(OH)·CH₂·CH·CH₂ (R = H, Me, Et, or ·CH·CH₂) at 340—360° in presence of Al₂O₃ are largely (50%) unaltered, a little H₂O and conjugated dienes are formed, and about 40% splits to give CH₂O, MeCHO, EtCHO, and acraldehyde, respectively, with CHMe·CH₂ in each case. CH₂Ph·CH₂·OH and CH₂Ph·CHMe·OH similarly afford CHPh·CH₂ and CHPh·CHMe, respectively.

J. L. D.

"Leaf alcohol." [*trans*-Δ²-hexenol]. I. Occurrence in plants. S. TAKEI, Y. SAKATO, M. ONO, and Y. KUROIWA. II. Synthetic perfumes from "leaf alcohol." S. TAKEI, M. ONO, Y. KUROIWA, T. TAKAHATA, and T. SIMA (J. Agric. Chem. Soc. Japan, 1938, 14, 709—716, 717—723).—I. The leaf oils from tea, ivy, clover, oak, wheat, mulberry, and black radish contain Δ²-hexenal with *trans*-Δ²-hexenol (I) (4'-iododiphenylurethane, m.p. 157°; 3:5-dinitrobenzoate, m.p. 49°; Ag salt of phthalic ester, m.p. 126°; allophanate, m.p. 146°; anthraquinone-2-carboxylate, m.p. 68°). In general

(I) occurs in the free state, but in Japanese peppermint oil it is present as the phenylacetate. Oxidation of (I) with CrO_3 gives the aldehyde (2:4-dinitrophenylhydrazones, m.p. 144°; semicarbazone, m.p. 173°).

II. (I) is converted into Δ^7 -hexenyl bromide by PBr_3 and condensation of this with acraldehyde yields $\alpha\zeta$ -nonadien- γ -ol (II) (4'-iododiphenylurethane, m.p. 122°; allophanate, m.p. 125°), which has an odour of cypress leaves or sea-cucumber. (II) by the successive action of PBr_3 , AgOBz , and KOH is converted into trans-trans- $\Delta^{8\epsilon}$ -nonadienol (4'-iododiphenylurethane, m.p. 137°; allophanate, m.p. 140°), which also has an odour of cypress leaves. Oxidation with CrO_3 yielded trans-trans- $\Delta^{8\epsilon}$ -nonadienol (semicarbazone, m.p. 157-5°; 2:4-dinitrophenylhydrazones, m.p. 113°) identical with the natural violet leaf aldehyde. Nonan- γ -ol (4'-iododiphenylurethane, m.p. 146°; allophanate, m.p. 135°) has a characteristic woody or Japanese lacquer odour. J. N. A.

Preparation of unsaturated alcohols by Grignard synthesis from α -diketones and allyl bromide. J. I. JUSCHTSCHENKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1938, 5, 101-113).— Ac_2 or benzil and Mg allyl bromide in Et_2O yield $\delta\epsilon$ -dimethyl-, m.p. 70-70.7°, or $\delta\epsilon$ -diphenyl-octa- $\Delta^{8\eta}$ -diene- $\delta\epsilon$ -diol, m.p. 141.5°. R. T.

Synthesis of adonitol. R. LESPIEAU (Compt. rend., 1938, 206, 1773-1775).—*dl*-Arabitol pentaacetate (I) synthesised as described previously (cf. A., 1936, 1229) is mixed with an oil which, when distilled in vac., affords some cryst. (I), which with boiling MeOH-HCl gives *dl*-arabitol (II), and an oil, hydrolysed (boiling MeOH-HCl) to adonitol (III). As all the OH in (III) are in the *cis*-positions to one another it follows that the OH in $\gamma\delta$ -trihydroxy- Δ^9 -pentinene (*loc. cit.*) are similarly related. The simultaneous formation of (II) and (III) is also explained on this assumption. No xylitol is isolated, but the considerable unworkable residues do not exclude its presence. J. L. D.

Hydrogenation of the furan nucleus in presence of Raney nickel. Application to the preparation of $\alpha\delta$ -epoxides (alkyltetrahydrofurans); $\alpha\delta$ -dibromides. R. PAUL (Bull. Soc. chim., 1938, [v], 5, 1053-1062).—Furylethylene, obtained by dicarboxylation of furylacrylic acid by quinoline containing anhyd. CuSO_4 , is hydrogenated (Raney Ni) to $\alpha\delta$ -oxido-*n*-hexane [η -ethyltetrahydrofuran], b.p. 108° (corr.)/758 mm.; reaction ceases when 90% of the calc. amount of H has been absorbed and the product is purified by cautious treatment with Br and final contact with K-Na. The mixture of furylpropane and -propene obtained by dehydration of furylethylcarbinol is similarly hydrogenated to $\alpha\delta$ -oxido-*n*-heptane [η -propyltetrahydrofuran], b.p. 135°/773 mm. $\alpha\delta$ -Oxido-*n*-octane, b.p. 159-160°/768 mm., and $\alpha\delta$ -oxido-*n*-nonane, b.p. 70-71°/14 mm., are described. Phenylfurylcarbinol is reduced (Na and abs. EtOH) to 2-benzylfuran, b.p. 104°/12 mm., hydrogenated (118°/65 atm.) to $\alpha\delta$ -oxido- ϵ -phenyl-*n*-pentane, b.p. 109-110°/10 mm. The requisite oxide is dissolved in AcOH and the solution is saturated with HBr at room temp. and then heated in a sealed tube

at 120-130°, whereby the following dibromides are obtained: $\alpha\delta$ -dibromo-*n*-heptane, b.p. 110-112°/11 mm.; $\alpha\delta$ -dibromo-*n*-octane, b.p. 125-126°/11 mm.; $\alpha\delta$ -dibromo-*n*-nonane, b.p. 139-140°/11 mm.; $\alpha\delta$ -dibromo- ϵ -phenylpentane, b.p. 153-155°/4 mm.

H. W.

Esterification of acetic acid at high pressure.—See A., 1938, I, 405.

Catalytic preparation of isoamyl acetate. IV. M. B. TUROVA-POLAK and L. A. VOROTNIKOVA (J. Appl. Chem. Russ., 1938, 11, 643-645).—The highest yield of $\text{C}_5\text{H}_{11}\cdot\text{OAc}$ from *iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$ and AcOH is obtained at 100-120° ($\text{C-H}_3\text{PO}_4$ catalyst). The yield falls abruptly as the temp. exceeds 170°, owing to dehydration of the alcohol to yield amylene.

R. T.

Preparation and properties of esters of β -methoxyisobutyl alcohol. L. E. THOMAS [with R. E. NELSON] (J. Org. Chem., 1938, 2, 506-507).— β -Methoxyisobutyl alcohol, the appropriate acid anhydride, and a little H_2SO_4 give, when warmed, the acetate, b.p. 162.7-162.8°/733.69 mm., 58-58.5°/15 mm., propionate, b.p. 176.1-176.7°/733.69 mm., 78-78.5°/20 mm., and butyrate, b.p. 193.4-193.5°/733.69 mm., 87.5-88°/20 mm. R. S. C.

Conversion of stearic acid into oleic acid by catalytic dehydrogenation. L. MARGAILLAN and X. ANGELI (Compt. rend., 1938, 206, 1662-1663).—Me stearate vapour in C_2H_4 when passed over reduced Ni at 220° affords some Me oleate (23%), H_2 , and C_2H_6 . The reaction proceeds in the liquid ester with C_{10}H_8 acting as a H acceptor, though less efficiently than in the vapour state. Me palmitate is not dehydrogenated similarly. J. L. D.

Dehydration of ricinoleic acid, and polymerisation of the triglyceride of $\Delta^{9\kappa}$ -octadecadiene-carboxylic acid. P. M. BOGATTREV, S. M. DRIDZE, and I. A. KUZIBERDIN (Prom. Org. Chim., 1938, 5, 327-333).—The action of metallic catalysts (Zn, Cu) in the dehydration of ricinoleic acid (I) (in castor oil) at 280° is ascribed to formation of fatty acid salts of these metals; the process is thus one of homogeneous catalysis. Both formation of these salts and subsequent formation and decomp. of *O*-esters of (I) to yield dienic acid glycerides (II) are ascribed to formation of acid products of thermolysis [chiefly $\text{C}_{11}\text{H}_{23}\cdot\text{CO}_2\text{H}$ (III)], the process being thus a special case of the Crafts reaction. Addition of acids accelerates the process, and lowers the yield of by-products [(III), $\text{C}_7\text{H}_{15}\cdot\text{CHO}$], in the following diminishing order of efficacy: oxalic, boric, phthalic, stearic, oleic, and abietic acid. Under optimal conditions >85% of the (I) content of castor oil is dehydrated. The (II) formed polymerises almost immediately. A structural formula, based on theoretical considerations, is proposed for the polymeride. R. T.

Fats. LXI. Constitution of parinaric acid. H. P. KAUFMANN, J. BALTES, and S. FUNKE (Fette u. Seifen, 1938, 45, 302-304).—The spectral absorption curve of recryst. parinaric acid, m.p. 83°, from the fat of *Parinarium laurinum*, in abs. EtOH shows max. at λ 320, 307, and 292 m μ . (log E = 4.5 to 4.8)

and is very similar to that of decatetraene; this evidence supports the formula $\text{Et} \cdot [\text{CH} \cdot \text{CH}]_4 \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$ (cf. Farmer and Sunderland, A., 1935, 1041). E. L.

Linoleic acid and its isomerides. J. W. McCUTCHEON (Canad. J. Res., 1938, 16, B, 158—175).—A prep. of fatty acids from sunflower seed oil is brominated by a modification of Rollett's method (A., 1909, i, 759) and the tetrabromide (I), m.p. 115.2° (yield 50%), of linoleic acid is isolated, free from the liquid isomeride (details given). (I) is debrominated with Zn and then boiled with 4N-HCl in EtOH to give Et linoleate, b.p. $212^\circ/12$ mm., hydrolysed at room temp. to linoleic acid (II), m.p. -8° to -9° [dimorphous form (?), m.p. -13° to -14°] (amide, m.p. $57-58^\circ$, decomposes slightly after some weeks to give an amber-coloured liquid). Pure (II) with Br in light petroleum at -10° to -2° affords (I) and a liquid tetrabromide, converted by debromination and esterification into Et linoleate, b.p. $215^\circ/12$ mm., identical with the product obtained from (I). The acids derived from the solid and liquid tetrabromides when oxidised with alkaline KMnO_4 and H_2O_2 -AcOH, respectively, yield two pairs of sativic acids, m.p. 173° and 155° and m.p. 146° and 126° (cf. A., 1935, 998), respectively, so that the linoleic acids derived from the isomeric tetrabromides are not *cis-trans*-isomerides. The structures of the two tetrabromides are discussed. The preps. of the different products are described in detail.

J. L. D.

Action of antimony trisulphide on hydroxy-acids. Y. VOLMAR and E. WEIL (Compt. rend., 1938, 206, 1904—1905; cf. A., 1934, 187).—0.1N solutions of $\text{OH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ and $\text{OH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ react with Sb_2S_3 under the conditions described by Volmar and Betz (A., 1933, 948) with elimination of H_2S . Sb_2S_3 reacts exactly like Sb_2O_3 and max. yields are obtained with equimol. proportions of the reactants. Sb_2S_3 and K tartrate afford tartar emetic in good yield. β -OH-acids do not react.

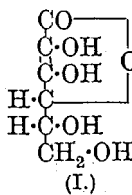
J. L. D.

Chemistry of the synthesis of acetoacetic ester. F. ARNDT and B. EISTERT (Ber., 1938, 71, [B], 1547—1549).—The acetoacetic ester synthesis comprises an initial, reversible phase in which the anion of the Na_1 compound of the "methylene component" is intruded into the "directed" CO group of the ester component and a second, irreversible phase in which a proton and [OR] anion are removed under the influence of more alkali and the eliminated R-OH is immediately transformed into NaOR. H. W.

Hydrogenation using colloidal rhodium. C. ZENGHELIS and K. STATHIS (Monatsh., 1938, 72, 58—62).—The rates of absorption of H_2 , using colloidal Rh in neutral solution at room temp. and atm. pressure, in the cases of COME_2 , C_6H_6 , PhNO_2 , PhCN , NH_2Ph , $\text{NPh} \cdot \text{NPh}$, and maleic, fumaric, and cinnamic acids, indicate the superiority of this catalyst to Ni and metals of the Pt group, under the conditions used. A. T. P.

Effect of chlorophyll on the autoxidation of ascorbic acid.—See A., 1938, III, 744.

Preparation, electrometry, and ultra-violet spectrography of *d*-araboascorbic acid. G. CARPÉNI (Compt. rend., 1938, 206, 1816—1818; cf. A., 1938, I, 399).—*d*-Araboascorbic acid (I), m.p. 164° ,



has been prepared from fructose, which is converted successively into β -diisopropylidene-fructose, K diisopropylidene- α -ketogluconate, Me α -ketogluconate, and the Na salt of (I). Electrometric titration of (I) gives $p_{K_1} = 4.23 \pm 0.02$, $p_{K_2} \sim 11-12$; *d*-oxyaraboascorbic acid, the I oxidation product of (I), has $p_{K_2} \sim 8.8$. The undissociated mol. of (I) and its uni- and bi-valent ions give absorption max. at 2420, 2645, and 2990 \AA ., respectively. These results show that the steric isomerism of *L*-ascorbic acid and (I) does not affect the properties of the enediol- α -keto-group.

A. J. E. W.

Preparation, electrometry, and ultra-violet spectrography of glucoheptoascorbic acid. G. CARPÉNI (Compt. rend., 1938, 206, 1376—1378).—

Glucoheptoascorbic acid (I) has been prepared from α -glucoheptose by successive conversion into the osazone, osone, and nitrile, followed by acid hydrolysis. (I) cannot be cryst. from aq. solution, probably owing to suppression of the growth of micro-crystals by traces of impurity. Electrometric titration of (I) gives $p_{K_1} = 4.30 \pm 0.05$, $p_{K_2} \sim 11-12$; the I oxidation

product of (I) has $p_{K_2} \sim 8.8$. Absorption max., λ_M (at 2430—2980 \AA .), of aq. solutions of (I) of different p_H are recorded; the inflexion in the λ_M - p_H curve corresponds with $p_{K_2} \sim 12$. The length of the C chain has little effect on the dissociation consts. and absorption spectra of the enediol- α -keto-group.

A. J. E. W.

Electrolytic preparation of calcium gluconate and other salts of aldonic acids. C. G. FINK and D. B. SUMMERS (Trans. Electrochem. Soc., 1938, 74, Preprint 7, 24 pp.).—An alkaline solution of glucose containing KBr or NaBr is electrolysed with a graphite anode and a graphite or Fe cathode, and the liquid neutralised with intermittent additions of CaCO_3 . The effect of variations in numerous factors has been investigated, the optimum conditions for a semi-plant scale being: 1M-glucose in 2% NaBr; c.d. 1—2 amp. per sq. dm.; 40° ; no diaphragm. Loss of Br, which normally increases with time, can be considerably reduced by changing the current direction approx. every 15 min. Salts of other acids can be prepared by electrolysing other aldoses. Salts other than KBr and NaBr were investigated but only KI and $\text{K}_3\text{Fe}(\text{CN})_6$ showed any considerable efficiency. Ca gluconate (I) can also be prepared by electrolysing a solution containing 20% of glucose and 5% of (I), using a Hg anode and a graphite cathode, at $96-100^\circ$, with a c.d. 1.2—1.4 amp. per sq. dm., and adding CaCO_3 intermittently.

C. R. H.

Peroxide effect in the addition of reagents to unsaturated compounds. XVI. Addition of thiolaetic acid to styrene and isobutene. M. S. KHARASCH, A. T. READ, and F. R. MAYO (Chem. and Ind., 1938, 752).—At room temp. in presence of

ascaridole, $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ gives (abnormally) with styrene, $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and with $\text{CMe}_2\cdot\text{CH}_2\cdot\text{SBu}^\beta\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, but in presence of $p\text{-C}_6\text{H}_4(\text{OH})_2$ in vac. it does not react with either. A chain mechanism for O_2 or peroxide catalysis is suggested.

A. Lr.

Reactions of formaldehydesulphoxylic acid. L. SPITZER (Annali Chim. Appl., 1938, 28, 227—229).—The Na salt with $\text{Hg}(\text{OAc})_2$ gives a black ppt. which is black or greenish-yellow after boiling and white with HCl (the colour change depending on the amount of reagent used); $\text{CH}_2\text{O}\cdot\text{NaHSO}_3$, however, gives a yellow solution and, on boiling, a reddish ppt. HgCl_2 is reduced to HgCl . CuSO_4 gives a green solution which deposits Cu on boiling; no ppt. of Cu is produced by $\text{CH}_2\text{O}\cdot\text{NaHSO}_3$.

F. O. H.

Purification of the alcoholate of the trimeride of hydroxypyruvaldehyde. W. E. EVANS, jun., C. J. CARR, and J. C. KRANTZ, jun. (J. Amer. Chem. Soc., 1938, 60, 1628—1629).— $\text{CO}(\text{CH}_2\cdot\text{OH})_2$ and $\text{Cu}(\text{OAc})_2$ give 64% of the pure, amorphous trimeride ($+\text{EtOH}$), m.p. 155—160°, of $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CHO}$, which gives the quinoxaline derivative, m.p. 250—251° (lit. 165°), and dioxime, m.p. 134—135° (lit. 168°).

R. S. C.

Keto-enol tautomerism in light and heavy (deuterium) solvents. F. C. NACHOD (Z. physikal. Chem., 1938, 182, 193—219).—The keto-enol equilibria of CH_2Ac_2 and CHMeAc_2 have been studied in H_2O and D_2O and in MeOH and MeOD . The proportion of enol is considerably reduced in D_2O as compared with H_2O . A similar though smaller reduction occurs in MeOD as compared with MeOH but for CH_2Ac_2 in these solvents it is within the limits of experimental error. The proportion of the keto-forms increases greatly in 0.1N-HCl in EtOH . The effect is considerably less in aq. acid. The solubilities of various org. compounds have been determined in H_2O and D_2O and the rate of enolisation of CHMeAc_2 has been studied in H_2O and EtOH . The differences between the rates for light substances in light solvents and heavy substances in heavy solvents are explained.

T. H. G.

Photochemical interaction between ketones and secondary alcohols.—See A., 1938, I, 408.

Photochemical interaction between ketones and alcohols. C. WEIZMANN, E. BERGMANN, and Y. HIRSHBERG (J. Amer. Chem. Soc., 1938, 60, 1530—1533).—When irradiated by a Hg arc, COPhMe and $\text{Bu}^\alpha\text{OH}$ give $\text{Pr}^\alpha\text{CHO}$ (50%) and both stereoisomeric forms of $(\text{CPhMe}\cdot\text{OH})_2$. The same pinacols are similarly obtained from COPhMe and cyclohexanol (I) [gives 80% of the ketone (II)] or $\text{CHPhMe}\cdot\text{OH}$. COMe_2 and Pr^βOH give $(\text{CMe}_2\cdot\text{OH})_2$. (I) and (II) give only a poor yield of cyclohexanonepinacol, which was not isolated, but its presence is inferred by conversion into dicyclohexenyl. COMe_2 and $\text{Bu}^\alpha\text{OH}$ give Pr^βOH , $\text{Pr}^\alpha\text{CHO}$ and its trimeride, and forms, m.p. 121° and b.p. 95°/0.3 mm., respectively, of octane-8s-diol. The reaction depends on the presence of H attached to C in $\text{CH}\cdot\text{OH}$, but this H is not detached during reaction as $\text{CHPhMe}\cdot\text{OH}$ is not racemised by irradiation. COPhMe and $d\text{-CHPhMe}\cdot\text{OH}$ give inactive pinacols, and reaction

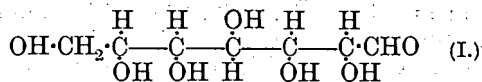
thus proceeds by activation of CORR' to $\cdot\text{CRR}'\cdot\text{O}\cdot$, formation of $\cdot\text{CRR}'\cdot\text{OH}$ (from the ketone) and $\cdot\text{CR}''\text{R}'''\cdot\text{OH}$ (from the alcohol), and finally symmetrical or asymmetrical dimerisation to the pinacol or further oxidation to a new ketone. Conversion of ergosterol in the presence of eosin into the pinacol similarly involves activation of the H at $\text{C}_{(3)}$.

R. S. C.

Keto-ethers. III. β -Halogenoethoxyethyl alkyl ketones derived from ethylene bromohydrin. J. H. CLARK [with H. R. HENZE] (J. Org. Chem., 1938, 2, 508—513; cf. A., 1937, II, 177).—Passing HCl into $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{OH}$ and $(\text{MeCHO})_3$ at 0° gives 69% of α -chloroethyl β -bromoethyl ether, b.p. 84.2°/37 mm., converted by CuCN , best in C_6H_6 , into α - β' -bromoethoxypropionitrile, b.p. 69°/3 mm., which with the appropriate Mg alkyl bromide affords *Me*, b.p. 63.5°/2 mm. [semicarbazone, m.p. 124.5° (decomp.)], and *Et* α - β' -bromoethoxyethyl ketone, b.p. 91°/6.5 mm. (semicarbazone, m.p. 99.5°), α - β' -bromoethoxyethyl n-, b.p. 82.5—83.5°/2.5 mm. (semicarbazone, m.p. 112.5°), and iso-propyl, b.p. 80—81°/2.5 mm., n-, b.p. 102—102.5°/4 mm. (semicarbazone, m.p. 117.7°), iso-, b.p. 91—92°/2 mm., and sec-butyl, b.p. 89.5°/2.5 mm., n-, b.p. 119.5—120°/5.5 mm. (semicarbazone, m.p. 106.3°), and iso-amyl ketone, b.p. 100.5—101°/2.5 mm. (semicarbazone, m.p. 83°). Temp. are corr.

R. S. C.

Suggestion for naming the higher carbon sugars. C. S. HUDSON (J. Amer. Chem. Soc., 1938, 60, 1537—1541).—It is suggested that $>\text{C}_6$ sugars should be named by relating the 4 $\text{CH}\cdot\text{OH}$ adjacent to the $\text{CH}_2\cdot\text{OH}$ and the 4 $\text{CH}\cdot\text{OH}$ adjacent to the CHO each to the appropriate hexose. *E.g.*, α -D- α -glucoheptose (I) is termed D-gluco-D-guloheptose. Numerous examples of naming heptoses, octoses, and



their derivatives on this system are given. 2-Ketoheptoses are named heptuloses. 7-Deoxyheptoses are best named methyloheptoses. The α - and β -nomenclature is retained only for glucosides. The disadvantages of other systems, particularly that of Isbell, are stressed.

R. S. C.

Preparation of 2 : 3-, 3 : 4-, and 3 : 6-anhydromethylhexosides from 3-p-toluenesulphonylmethylglucoside. S. PEAT and L. F. WIGGINS (J.C.S., 1938, 1088—1097).—Alkaline hydrolysis of β -methylglucoside 3-p-toluenesulphonate to anhydrosugars proceeds partly with and partly without Walden inversion. Inversion accompanies alkaline fission of dimethyl-3 : 4-anhydro- β -methylalloside. Hydrolysis of sugar p-toluenesulphonates may occur without anhydro-ring formation, but in these cases no inversion occurs. isoPropyrideneglucose 3-p-toluenesulphonate and hot 2% $\text{HCl}\cdot\text{MeOH}$ give a mixture of glucosides (A), converted by $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ at 36° or $\text{NaOAc}\cdot\text{Ac}_2\text{O}$ into β - (I), m.p. 138°, $[\alpha]_D^{20} -19.5^\circ$ in CHCl_3 (cf. Freudenberg and Ivers, A., 1922, i, 523), and α -methylglucoside 2 : 4 : 6-triacetate 3-p-toluenesulphonate, m.p. 97°, $[\alpha]_D^{20} +87.1^\circ$ in CHCl_3 . With $\text{NaOMe}\cdot\text{MeOH}\cdot\text{CHCl}_3$ at room temp. (I) gives a

mixture, $[\alpha]_D^{20} -80^\circ$ to -90° in EtOAc, which with PhCHO and P_2O_5 in $CHCl_3$ gives 4:6-benzylidene-2:3-anhydro- β -methylalloside, m.p. 138° , $[\alpha]_D^{19} -15.6^\circ$ in $CHCl_3$, and a syrup, converted by MeI- Ag_2O into 2:6-dimethyl-3:4-anhydro- β -methylalloside (II), m.p. 46° , $[\alpha]_D^{21} -144.5^\circ$ in $CHCl_3$, and impure 2:4-dimethyl-3:6-anhydro- β -methylglucoside (III). (II) and 5% NaOMe-MeOH at 95° give 2:3:6-trimethyl- β -methylglucoside (IV), m.p. $59-60^\circ$, $[\alpha]_D^{19} -48^\circ$ in $CHCl_3$, $[\alpha]_D^{17} -33.4^\circ$ in H_2O , and impure, oily 2:4:6-trimethyl- β -methyl-d-gulopyranoside (V). Three methylations of (IV) with Ag_2O -MeI give tetramethyl- β -methylglucopyranoside, hydrolysed to tetramethyl- α -d-glucopyranose. Hydrolysis of (IV) gives 2:3:6-trimethylglucose, oxidised by Br to trimethylgluconic acid. Methylation of (V) gives a tetramethyl- β -methylhexoside, b.p. $85-90^\circ$ (bath)/0.01 mm., $[\alpha]_D^{17} -69^\circ$ in $CHCl_3$, hydrolysed by 6% HCl to tetramethyl-d-gulose, an oil, $[\alpha]_D^{18} +8.25^\circ$ in H_2O , which with Br gives tetramethyl-d-gulonolactone, $[\alpha]_D^{18} +64.6^\circ \rightarrow +22^\circ$ in H_2O in 32 hr. (very rapid hydrolysis indicates the δ -lactone structure), oxidised by HNO_3 to i -(OMe-CH-CO $_2$ H) $_2$ and l -arabotrimethoxyglutaric acid; these products all contained some of the derivatives from (V) and i -trimethoxyxyloglutaramethylamide, m.p. 166° , was incidentally isolated. The pyranoside structure of (V) is also supported by its rapid hydrolysis by HCl. Purification of (III) by further methylation, acetylation, and distillation gives an oil, $[\alpha]_D^{15} -1.68^\circ$ in $CHCl_3$; this is stable to 2.5N-KOH in 75% EtOH, is merely converted into the α -glucoside by hot 6% HCl-MeOH, but with cold, dil. aq. HCl yields 2:4-dimethyl-3:6-anhydroglucose (VI), $[\alpha]_D^{18} -1.1^\circ \rightarrow +61.9^\circ$ in 300 hr. (VI) gives the anilide, m.p. 96° , and with Br affords 2:4-dimethyl-3:6-anhydrogluconolactone, $[\alpha]_D^{18} +90.9^\circ \rightarrow +64.2^\circ$ in H_2O in 180 hr., yielding 2:4-dimethyl-3:6-anhydrogluconamide, m.p. $91-92^\circ$. The mixture (A), when hydrolysed by NaOMe at room temp. and then methylated, yields a mixture, containing 4:6-dimethyl-2:3-anhydro- α -methylalloside, m.p. 63° , $[\alpha]_D^{18} +187^\circ$; the crude hydrolysis product yields 4:6-ethylidene-, m.p. 128° , $[\alpha]_D^{18} +100^\circ$ in $CHCl_3$, and 4:6-benzylidene-2:3-anhydro- α -methylalloside, m.p. 198° , $[\alpha]_D^{20} +161^\circ$, the latter product giving by H_2 -Pd-C in EtOH-COMe $_2$ at 1.5 atm. 2:3-anhydro- β -methylalloside, m.p. $60-62^\circ$, $[\alpha]_D^{17} -6.1^\circ$ in EtOAc, hygroscopic (4:6-Me $_2$, m.p. $50-51^\circ$, $[\alpha]_D^{19} +35.3^\circ$ in $CHCl_3$, and 4:6-benzylidene derivative, m.p. 188° , $[\alpha]_D^{19} -62.9^\circ$ in COMe $_2$). β -Methylglucoside 3:4:6-triacetate 2- p -toluenesulphonate and NaOMe give 2:3-anhydro- β -methylmannoside, $[\alpha]_D^{19} -28.8^\circ$ (4:6-benzylidene derivative, m.p. 183° , $[\alpha]_D^{19} -30.7^\circ$ in $CHCl_3$). 5% HCl at 95° (not room temp.) converts 4:6-dimethyl-2:3-anhydro- α -methylalloside into a chlorodimethylhexose, $[\alpha]_D^{20} +67.5^\circ$ in 5% HCl, but (II) is hydrolysed in the cold to an oily chlorodimethylhexose, $[\alpha]_D^{20} -76.6^\circ$ in 5% HCl (yields an oily chlorodimethylmethylhexoside acetate, $[\alpha]_D^{20} -41.4^\circ$ in $CHCl_3$). *iso*Propyrideneglucose 3- p -toluenesulphonate or 1:2-*iso*propyrideneglucofuranose 5:6-diacetate 3- p -toluenesulphonate (VII) with cold NaOMe give slowly *iso*propyrideneglucose without anhydro-ring formation or inversion. Attempts to replace the $ArSO_2$ of (VII) by Ac failed.

R. S. C.

Pyranose-furanose interconversions with reference to the mutarotations of galactose, α -lactulose, lactulose, and turanose. H. S. ISBELL and W. W. PIGMAN (J. Res. Nat. Bur. Stand., 1938, 20, 773-798).—Measurements of $[\alpha]$, mol. vol., and mol. refraction in buffered solutions show that the mutarotations of α -lactulose (I) (pyranose form of d -fructose), lactulose (II), and turanose (III) are similar to the rapid mutarotation reactions of α - d -galactose and other sugars. The large variation of $[\alpha]$ with temp., the comparable heats of reaction, and the high sensitivity of the reaction rates to acids and bases confirm this. Since the fructose liberated from sucrose by invertase has a mutarotation rate equal and opposite to that of (I), it is concluded that these reactions are furanose-pyranose interconversions, that (II) is a furanose, and that the O-bridge of (III) is not attached to the 5th or 6th C, but probably (since the osazone differs from those of maltose and cellobiose) to the 3rd. A. LI.

Biochemistry of carbohydrates. XXXI. Determination of acetyl groups in carbohydrate complexes by the Friedrich-Rapoport-Sternberg method. Hydrolysis of ethereal sulphate. M. SUZUKI. XXXII. Glucosamine and chondrosamine. H. HISAMURA and M. KUSUNO (J. Biochem. Japan, 1938, 27, 367-373, 375-379).—XXXI. Improvements in the method are suggested (cf. A., 1936, 968). The liberation of SO_4^{2-} from chondroitin-sulphuric acid in N-HCl at 100° requires at least 7 hr. for completion.

XXXII. Glucosamine yields a Bz $_5$ derivative, m.p. 216° (corr.), $[\alpha]_D^{15} +45.06^\circ$ in C_5H_5N (cf. Levene, A., 1916, i, 713). Pentabenzoylchondrosamine, m.p. $199-201^\circ$, $[\alpha]_D^{22} +95.82^\circ$ in C_5H_5N , was also prepared. Glucosamine prepared by Breuer's method (A., 1898, i, 620) is the β -isomeride, the hydrochloride of which has initial (extrapolated) $[\alpha]_D^{17} +20.0^\circ$ in H_2O .

F. O. H.

Formation of diisopropylideneglucose diethyl mercaptal. Kinetics of the reaction. R. SUTRA (Bull. Soc. chim., 1938, [v], 5, 1048-1052).—Diisopropylidene- d -glucose Et $_2$ mercaptal is obtained as a non-distillable liquid, $[\alpha]_{578} -47.5^\circ$ in COMe $_2$, by the action of COMe $_2$ containing H_2SO_4 and anhyd. $CuSO_4$ on d -glucose Et $_2$ mercaptal. The product formed has at first an anticatalytic effect on the change which, subsequently, is of the first order. H. W.

Oxidation of methylated derivatives of sorbose with nitric acid. (MME.) Y. KHOUVINE and G. ARRAGON (Compt. rend., 1938, 206, 1659-1661).—Oxidation of α -tetramethyl- l -sorbose with HNO_3 affords d -dimethoxysuccinic acid (cf. A., 1937, II, 485). α - or β -Tetramethyl- l -sorbose or α - or β -tetramethyl- l -methylsorbose with HNO_3 (d 1.49) (conditions described) at 100° affords $H_2C_2O_4$ (removed with H_2O_2) and a syrup which when methylated (MeI- Ag_2O followed by Me $_2SO_4$) and fractionally distilled at 10^{-4} mm. gives fractions converted by NH_2Me into d -dimethoxysuccinmethylidamide and xylotrimethoxyglutarmethylidamide. The latter indicates the existence of a pyranoid structure in the original sugars. α - l -Methylsorbose tetra-acetate, α - l -methylsorbose, and α - l -sorbose have pyranoid

structures as the last can be converted into the first two. J. L. D.

Oxidation of tetramethyl- α -*d*-methyltagatose with nitric acid. (MME.) Y. KHOUVINE, G. ARRAGON, and Y. TOMODA (Compt. rend., 1938, 206, 1823—1824).— α -*d*-Methyltagatose (I) with Me_2SO_4 -NaOH at 60° affords tetramethyl- α -*d*-methyltagatose (II) (cf. A., 1938, II, 84) which with HNO_3 (*d* 1.49) at room temp. and then at 100° affords $\text{H}_2\text{C}_2\text{O}_4$ and an oil converted by MeI - Ag_2O and by Me_2SO_4 into an oil which when fractionally distilled affords *l*-dimethoxysuccindi(methylamide) and *d*-arabtrimethoxyglutardi(methylamide), indicating that (I) and (II) have pyranose structures.

J. L. D.

Catalytic hydrogenation of disaccharides. I. Cane sugar. T. TANNO (Bull. Inst. Phys. Chem. Res. Japan, 1938, 17, 447—472).—Sucrose (I) with H_2 under high pressure and reduced Ni at 170—175° affords *d*-mannitol (II) and *d*-sorbitol (III) in equal amounts corresponding with 25% of (I), glycerol (IV), and $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ (V). At 155—160°, (II), (III), and a syrup are formed. With fructose (VI) at 170—175°, (II) and (III) only are rapidly formed, which indicates that (IV) and (V) are formed because of the glucosido-group in (I) and further that (I) is converted into (VI) during the reaction. J. L. D.

Theory of mutarotation; mutarotation and catalytic hydrogenation of the glucosides of secondary amines. R. KUHN and L. BIRKOFER (Ber., 1938, 71, [B], 1535—1541).—Contrary to expectation, the glucosides of piperidine (I) and $\text{NH}(\text{CH}_2\text{Ph})_2$ are mutarotatory and, although the possibility of its passage into a Schiff's base is excluded, piperidine-*d*-glucoside is reduced (Ni) at 75° to *N*-1'-sorbitylpiperidine, m.p. 115—116°, $[\alpha]_D^{25} -22^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (penta-acetate, b.p. 145—150°/10⁻³ mm.). At 100° (Ni) piperidine-*d*-glucoside undergoes reductive fission to (I) and sorbitol. The rate of mutarotation is very greatly increased by the addition of small amounts of H_2O . The relationship is diametrically opposed to that of the glucosides of other sec. amines. Addition of H_2O probably occurs and the cations undergo transformation. These can pass into ammonium bases (salts) which contain the double linking essential to mutarotation and hydrogenation. The rate of mutarotation is more markedly influenced by traces of HCl than of H_2O . Apparently the basicity of the amine is important. Ring-double linking desmotropy is therefore the essential of mutarotation. The formation of Schiff's bases and of CO-compounds (keto-cyclo desmotropy) are individual cases subordinate to the main principle. H. W.

2-Naphthylamine- α -glucoside. V. CUCULESCO (Bull. Soc. chim., 1938, [v], 5, 970—973).—Glucose and β - $\text{C}_{10}\text{H}_7\text{NH}_2$ in boiling MeOH or EtOH afford 2-naphthylamine- β -*d*-glucopyranoside (+1 H_2O), m.p. (indef.) 113—114.5° (decomp.), $[\alpha]_D^{25} -136.3^\circ \pm 0.7^\circ$ diminishing slowly on account of decomp. It cannot be obtained anhyd. since loss of H_2O under diminished pressure is accompanied by decomp. It is transformed by $\text{C}_5\text{H}_5\text{N}$ and Ac_2O into 2-naphthylamine- β -*d*-glucopyranoside 2:3:4:6-tetra-acetate, m.p. 172.5—173°, $[\alpha]_D^{25} -114.0^\circ \pm 0.7^\circ$; also obtained from

β - $\text{C}_{10}\text{H}_7\text{NH}_2$ and acetobromoglucose in CCl_4 containing Ag_2CO_3 . H. W.

Fruit of *Sophora japonica*, L. I. Sophoricoside. C. CHARAUX and J. RABATÉ. II. Rutoside and sophoraflavanoloside. III. Holodiglucoside from sophoraflavanoloside. J. RABATÉ and J. DUSSEY (Bull. Soc. Chim. biol., 1938, 20, 454—458, 459—466, 467—470).—I. The green fruit contains 2% of a glucoside, *sophoricoside*, m.p. 297.5°, $[\alpha]_D^{20} -32.2^\circ$ in $\text{C}_5\text{H}_5\text{N}$, -46.7° in 0.02N-NaOH (hexa-acetate, m.p. 230°). Since hydrolysis by dil. H_2SO_4 in presence of AcOH yields 43.8% of glucose and 60.8% of genisteol, it is a β -glucoside of genisteol which differs in its physical constns. from genistin.

II. In addition to *sophoricoside*, extracts of the fresh fruit contain 0.6% of both *rutoside*, a heteroside, m.p. 202—203°, $[\alpha]_D^{20} -30^\circ$ in 50% EtOH, which yields glucose, rhamnose, and quercetin on hydrolysis with 3% H_2SO_4 , and *sophoraflavanoloside* (I), m.p. 207—208°, $[\alpha]_D^{20} -61^\circ$ (for anhyd. product), which yields glucose and kaempferol on hydrolysis with 3% H_2SO_4 .

III. *Sophorose*, a reducing α -diglucoside (+1 H_2O), has been obtained by hydrolysis of (I) with 0.5% H_2SO_4 . It has m.p. 195—196°, $[\alpha]_D^{20} +37^\circ \rightarrow +22.6^\circ$; and yields glucose on further hydrolysis with 1.5% H_2SO_4 . It does not form a typical osazone.

P. G. M.

Dextran synthesised by *Leuconostoc dextranicus*.—See A., 1938, III, 699.

Röntgenographic investigation of Schardinger's α -dextrin. O. KRATKY and B. SCHNEIDMESSER (Ber., 1938, 71, [B], 1413—1414).—The results confirm Freudenberg's conception of the presence of a large ring with five glucose residues. H. W.

Exchange reaction between cellulose and heavy water. Hydration of cellulose. G. CHAMPETIER and R. VIALARD (Bull. Soc. chim., 1938, [v], 5, 1042—1048).—Ash-free filter-paper, cotton linters cellulose, and mercerised cotton linters cellulose have been immersed in 99.55% D_2O at temp. between 10° and 100° and the exchange has been measured from the diminution of *d* of the liquid. Invariably the change involves 3 OH per glucose unit, thus justifying the view that the D_2O has penetrated into the interior of the cellulose. Simple superficial adsorption on the micelles could only occasion an exchange reaction with the OH groups in contact with the D_2O and consequently the no. of H exchanged would be <3 per glucose unit. These results confirm the formulæ $2\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{H}_2\text{O}$ assigned previously to the hydrates of ordinary and mercerised cellulose respectively. H. W.

Separation of small amounts of racemic amino-acids into their optical antipodes through the salts of cholestenonesulphonic acid. G. TRIEM (Ber., 1938, 71, [B], 1522—1524).—The NH_2 -acid is treated with cholestenonesulphonic acid in EtOH. The salt thus produced is triturated with PbO and then shaken with H_2O . Pb cholestenonesulphonate is filtered off, the filtrate is treated with H_2S and C, filtered, and the filtrate is evaporated at a low temp. The resolution of *dl*-leucine, *dl*-

α -aminobutyric acid, *dl*-tyrosine, and (in part) that of *dl*-aspartic acid has been achieved. *d*(-)-*Leucine cholestenonesulphonate* has m.p. 192–193° (decomp.).

H. W.

N-Methanesulphonyl derivatives of amino-acids. B. HELFERICH and R. MITTAG (Ber., 1938, 71, [B], 1480–1482).— $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and MeSO_2Cl in abs. Et_2O afford *Et methanesulphonamidoacetate*, m.p. 42.5° (corr.), hydrolysed by 2N-NaOH to *methanesulphonamidoacetic acid*, m.p. 174° (corr.); also obtained directly from $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and MeSO_2Cl in presence of 2N-NaOH; it gives a Na salt, m.p. 220°. *Et* α -methanesulphonamidopropionate, b.p. 166°/4 mm., 140°/0.3 mm., and α -methanesulphonamidopropionic acid, m.p. 80°, are described.

H. W.

Separation of diketopiperazines and amino-acids in the products of the hydrolysis of proteins by ionophoresis. III. N. I. GAVRILOV, A. I. PARADASCHVILI, V. S. BALABUSHA-POPOVA, and S. W. LJAPOUNZOVA. IV. V. S. BALABUSHA-POPOVA, N. I. GAVRILOV, A. I. PARADASCHVILI, and G. F. JAKUNIN (Bull. Soc. chim., 1938, [v], 5, 973–978, 978–986).—III. Histidine anhydride passes entirely to the cathode without being decomposed and at a rate approaching that of the transport of free histidine. Hydrolysis or deamination does not occur. Aspartic anhydride under the experimental conditions (CO_2 at cathode) behaves like glycine anhydride and scarcely dissociates. At the conclusion of the experiment it cannot be detected at the anode and only traces of it are present in the cathode liquor. Tyrosine passes to the cathode and, to a smaller extent, to the anode, where it becomes oxidised. An agar diaphragm completely inhibits its transport to the anode. Deamination of glycine at a Ag cathode increases only the quantity of NH_3 ; it is due to an unsuitably high c.d. Prolongation of ionophoresis causes loss of N in other forms, evidently at the anode. The Ag cathode has not sp. deaminating properties but all those processes which occur at a Hg cathode are manifested in a greater degree. Mineral acid increases appreciably the production of NH_3 at the cathode.

IV. During ionophoresis of hexonic bases, of valine, and of glutamic and aspartic acid the c.d. should not exceed 10–15 ma. per sq. cm. The cathodic solution should be kept acid by a stream of CO_2 ; addition of mineral acid at the cathode increases the deamination of NH_2 -acids. Aspartic acid migrates very slowly towards the cathode. In this case the customary acidification of the solution is inadequate; more powerful acidification is required and this involves a certain amount of deamination. Dipeptides during ionophoresis pass entirely to the cathode without being hydrolysed. If the conditions favourable for the ionophoresis of dipeptides are maintained (initial acidification with 0.1N- H_2SO_4 and passage of CO_2 through the cathodic solution) there is no liberation of NH_3 in the cathodic liquor at c.d. 10 ma. If the c.d. increases to 35–40 ma. per sq. cm. an insignificant deamination results; this is betrayed by the formation of small amounts of NH_3 . H. W.

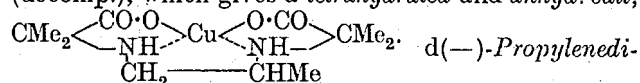
Hydrolysis of peptides of diaminosuccinic acid. T. TAMURA (J. Biochem. Japan, 1938, 27, 335—

M* (A., II.)

349).—*meso*-Diaminosuccinic acid (Et_2 ester *dihydrochloride*, m.p. 178°; Bz_2 derivative, m.p. 212°) with $\text{CH}_2\text{Cl}\cdot\text{COCl}$ gives *meso-dichloroacetamidossuccinic acid*, m.p. 205° [Et_2 ester (I), m.p. 156°], converted by NH_3 into *meso-diaminoacetamidossuccinic acid* (II), m.p. 275° (decomp.) [corresponding *dl*-compounds, m.p. 208° (Et_2 ester, m.p. 142°) and 245° (decomp.), respectively]. (I) with $\text{EtOH}\cdot\text{NH}_3$ affords *diglycyl-meso-diaminosuccinic anhydride*, m.p. 183° (corresponding *dl*-compound, m.p. 167°). *dl*-Dibenzamidossuccinic acid, m.p. 152°, was also prepared. (II) is readily hydrolysed by erepsin (aminopolypeptidase action) and trypsin, but only slightly by papain. The above dibenzoyl-*meso*- and -*dl*-acids, and also benzoyl-aspartic and -glutamic acids, are not hydrolysed by histozyme. The anhydrides are not hydrolysed by proteases, due to non-dissociation of the ketopiperazine side-chains. Glycyl- and aspartyl-aspartic anhydrides are readily hydrolysed by glycerol extracts of dried pig's pancreas. The bearing of the results on the structure of the above compounds and on the related enzyme actions is discussed.

F. O. H.

Complex salts of alkylenedi- α -amino-acids. P. PFEIFFER and W. CHRISTELEIT (Ber., 1938, 71, [B], 1497–1504).—*dl*-Propylenediamine hydrochloride, KCN, and COMe_2 in H_2O give the corresponding dinitrile, hydrolysed (fuming HCl -conc. H_2SO_4 at 0°) to *dl-propylenedi- α -aminoisobutyric acid*, m.p. 378° (decomp.), which gives a *tetrahydrated* and *anhyd. salt*,



α -aminoisobutyric acid, $[\text{M}]_{\text{D}_{25}}^{21} - 2.8^\circ$ in H_2O (other vals. recorded), gives a violet dehydrated and a blue anhyd. Cu salt, showing a pronounced Cotton effect. The compounds, $\text{C}_{11}\text{H}_{20}\text{O}_4\text{N}_2\text{Cu} + \text{EtOH}$, + $2\text{CH}_2\text{Ph}\cdot\text{OH} + \text{EtOH}\cdot\text{H}_2\text{O}$ and + $\text{PrOH}\cdot\text{H}_2\text{O}$, are also described. The violet Cu salt of heptamethylenedi- α -aminoisobutyric acid contains rather > 1 H_2O and gives a violet, anhyd. salt. Schlesinger's isomeric blue salt appears to contain 1 H_2O + 1 EtOH. *Diacetamidoheptamethylene* has m.p. 118°.

* H. W.

Possibility of the formation of cyclols from simple peptides. K. H. MEYER and W. HOHENEMSER (Nature, 1938, 141, 1138–1139).—Glycyl-*l*-leucine and *l*-leucylglycine show no interchange of their constituent groups on mixing. Under the given conditions cyclol formation does not occur. This does not support the cyclol theory of Wrinch (A., 1937, 11, 475; III, 296).

L. S. T.

Multivalent amino-acids and peptides. X. Cystinyl peptides as substrates for aminopolypeptidase and dipeptidase. (Miss) J. P. GREENSTEIN (J. Biol. Chem., 1938, 124, 255–262).—Cystinylpeptides which yield an insol. NH_2 -acid which can be filtered off and determined are convenient for determining peptidases. Glycine anhydride in 2N-NaOH and dicarbobenzyloxycystinyl chloride (adding 1N-NaOH) give *dicarbobenzyloxy-l-cystinylbisdi-glycine*, m.p. 210°; this is reduced by Na in liquid NH_3 (cf. A., 1935, 1486), treated with H_2SO_4 and then with HgSO_4 reagent, and the Hg salt decom-

posed by H_2S , and $\text{Ba}(\text{OH})_2$ added. The resulting solution is oxidised by air (Fe_2O_3) to give, after removal of BaSO_4 and addition of EtOH , *cystinylbis-diglycine* (I), m.p. (+ $2\text{H}_2\text{O}$) 98° , anhyd. 145° , $[\alpha]_D^{20} -55^\circ$ in 1N-HCl , hydrolysed by 5N-HCl to cystine, $[\alpha]_D^{20} -202^\circ$ (showing that little or no racemisation occurs during synthesis). Aminopolypeptidase or crude erepsin at 30° hydrolyses (I) to cystine [in a new cryst. form (hexagonal prisms)], which is collected and determined; the amount remaining in solution is negligible. *l*-Cistinyl diglycine is also hydrolysed by erepsin, but only partly by aminopolypeptidase. Neither peptide is hydrolysed by carboxypeptidase; this, however, hydrolyses chloroacetyltyrosine to tyrosine, which may be filtered off and determined. E. W. W.

Physiological specificity of methionine in regard to the methylthiol group: synthesis of *S*-ethylhomocysteine (ethionine) and its availability for growth. H. M. DYER (J. Biol. Chem., 1938, 124, 519—524).— α -Amino- γ -ethylthiolbutyric acid [ethionine], m.p. 272° (*N*- PhSO_2 derivative, m.p. 80°), does not support growth of animals on a cystine-deficient diet, and appears to be toxic to rats.

J. N. A.

ψ -Halogens. XXXIV. Reaction of hydrogen thiocyanate with cyanic acid and isothiocyanatoformamide. L. BIRCKENBACH and K. KRAUS (Ber., 1938, 71, [B], 1492—1497).—Pure HCNS and pure NH_4CO do not react at -80° or at -15° but in Et_2O at 0° give thiocyanatoformamide (I), m.p. 69° , which is stable in the absence of moisture but is decomposed by warm H_2O into CO_2 and NH_4CNS . It is transformed by EtOH into *Et thioallophanate*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$, decomp. 180° , which gives $\text{CO}(\text{NH}_2)_2$ and $\text{CS}(\text{NH}_2)_2$ when heated with NH_3 , passes into EtCNS when heated alone, and affords *O*-ethylisobiuret, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{OEt}$, m.p. $126-127^\circ$, with EtOH-NH_3 . With NH_2Ph (I) immediately yields *1-phenyl-2-thiobiuret*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, m.p. 161° , transformed by AgNO_3 into phenylbiuret and almost quantitatively converted by conc. aq. NH_3 into $\text{NHPh}\cdot\text{CS}\cdot\text{NH}_2$ and $\text{CO}(\text{NH}_2)_2$. H. W.

ψ -Halogens. XXXV. Cyanic acid. II. Cyanic and sulphuric acids. M. LINHARD (Annalen, 1938, 535, 267—284).— $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (1 mol.) and HNCO (1 mol.) in abs. Et_2O at -60° to -50° give mainly cryst. *carboxyaminosulphonic acid*, $\text{CO}_2\text{H}\cdot\text{NH}\cdot\text{SO}_3\text{H}$, which spontaneously loses CO_2 to give $\text{NH}_2\cdot\text{SO}_3\text{H}$. 2 mols. of HNCO and 1 mol. of H_2SO_4 give primarily $\text{SO}_2(\text{NH}\cdot\text{CO}_2\text{H})_2$, which loses 1 CO_2 to give $\text{NH}_2\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CO}_2\text{H}$ (also obtained to some extent from 1 mol. of each reagent). This product reacts usually rather as *carbamidosulphonic acid*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{SO}_3\text{H}$, and probably has the zwitterion structure, $\text{NH}_2\cdot\text{NH}_3^+\text{CO}_2\text{SO}_3^-\text{NH}\text{CO}_2\text{H}$. (I) gives an NH_4 , m.p. 168° (decomp.) [hydrolysed by hot $\text{N-H}_2\text{SO}_4$ to $(\text{NH}_4)_2\text{SO}_4$ and $\text{CO}(\text{NH}_2)_2$], *K*, m.p. 201° (decomp.), NH_4Et , m.p. 156° (decomp.), and NH_4Et salt, m.p. 130° , (I) reacting in these cases as $\text{CO}\cdot\text{NH}_3^+\text{NH}\text{SO}_2\text{CO}_2\text{H}$. With the weaker base, NH_2Ph , (I) gives NH_4 phenyl-

carbamidosulphonate, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{SO}_3\text{NH}_4$, decomp. about 135° , converted by KI into the *K* salt, $+\text{H}_2\text{O}$, decomp. about 137° , which with hot 17% HCl yields KHSO_4 and $\text{NHPh}\cdot\text{CO}\cdot\text{NH}_2$. With PhOH (I) gives NH_4 phenylurethanesulphonate, $\text{OPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{SO}_3\text{NH}_4$, rapidly converted by EtOH into NH_4EtSO_4 , $\text{OPh}\cdot\text{CO}\cdot\text{NH}_2$, HNCO , and PhOH . EtOH , Bu^nOH , Bu^iOH , and Bu^tOH give the NH_4 alkyl sulphate and alkylurethane. NH_4 *Bu*ⁿ sulphate melts at 222° . With H_2O (I) gives much CO_2 , HNCO , and NH_4HSO_4 , but in Et_2O slow addition of H_2O gives 80—90% of $(\text{NH}_4)_2$ carbamidodisulphonate, $\text{CO}(\text{NH}\cdot\text{SO}_3\text{NH}_4)_2$, $+\text{H}_2\text{O}$, decomp. $90-100^\circ$. The mechanism of the addition of HNCO and H_2SO_4 is discussed.

R. S. C.

Diacylcarbamides. I. Preparation and properties of diacylcarbamides derived from normal aliphatic acids. R. W. STOUTON (J. Org. Chem., 1938, 2, 514—521).— $\text{CO}(\text{NH}_2)_2$, EtCO_2H , and a little H_2SO_4 at 100° give exothermally *propionylcarbamide*, m.p. $210-211^\circ$. Adding the appropriate acyl chloride to $\text{CO}(\text{NH}_2)_2$ and 2 drops of H_2SO_4 in boiling C_6H_6 gives acetyl-, m.p. $216-217^\circ$, *n*-butyryl-, m.p. $173-174^\circ$, -octoyl-, m.p. $191-192^\circ$, -valeryl-, m.p. $182-183^\circ$, -hexoyl-, m.p. $192-193^\circ$, and -heptoyl-carbamide, m.p. $191-192^\circ$. Heating the appropriate acylcarbamide, acyl chloride (best the lower member of the pair; the anhydride gives lower yields), and a little H_2SO_4 in C_6H_6 gives 75—85% yields of *N*-acetyl-*N'*-propionyl-, m.p. $112-113^\circ$, -*N'*-butyryl-, m.p. $80-81^\circ$, -*N'*-valeryl-, m.p. $66-67^\circ$, -*N'*-hexoyl-, m.p. $85-86^\circ$, -*N'*-*n*-heptoyl-, m.p. $80-81^\circ$, and -*N'*-octoyl-carbamide, m.p. $92-93^\circ$, *N*-propionyl-*N'*-butyryl-, m.p. $96-97^\circ$, -*N'*-valeryl-, m.p. $82-83^\circ$, and -*N'*-heptoyl-carbamide, m.p. $82-83^\circ$, *N*-butyryl-*N'*-valeryl-, m.p. $75-76^\circ$, *N*-butyryl-*N'*-octoyl-, m.p. $66-67^\circ$, *N*-valeryl-*N'*-*n*-hexoyl-, m.p. $80-81^\circ$, *s*-dipropionyl-, m.p. $105-106^\circ$, *s*-dibutyryl-, (I), m.p. $86-87^\circ$, *s*-divaleryl-, m.p. $83-84^\circ$, *s*-di-*n*-hexoyl-, m.p. $87-88^\circ$, and *s*-di-*n*-heptoyl-carbamide (II), m.p. $89-90^\circ$. The diacylcarbamides are hydrolysed by hot (not cold) H_2O , slowly by acids, and very rapidly by alkali (in which they dissolve), the acyl of lower mol. wt. being most readily removed. With NaOEt at room temp. (I) gives NaCNO , $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{COPr}$, and PrCO_2Et . At $160-200^\circ$ (II) decomposes as to two thirds into CO_2 , $\text{C}_6\text{H}_{13}\cdot\text{CN}$, and $\text{C}_6\text{H}_{13}\cdot\text{CO}\cdot\text{NH}_2$, and one third into $\text{NH}(\text{COPr})_2$ and $(\text{HCNO})_3$. When injected intravenously into white mice, the diacylcarbamides have hypnotic, sedative, and analgesic action without causing excitement. The C_6-C_8 compounds are most potent, the min. effective dose being 80—150 mg. per kg. of body wt. Anaesthesia is, however, very short (mean 1—2 min.), probably owing to hydrolysis, and intraperitoneal and oral administration are, perhaps for this reason, much less effective. The min. lethal dose is about 2—3 times the effective dose. M.p. are corr.

R. S. C.

Synthesis of a radioactive organic compound: α -glycerophosphoric acid. E. CHARGAFF (J. Amer. Chem. Soc., 1938, 60, 1700—1701).—Radioactive P, obtained by bombarding CS_2 with fast neutrons and evaporating the product, is mixed

with red P, converted into radioactive PCl_3 and thence into radioactive POCl_3 (by KClO_3), isopropylidene-glycerophosphoric, and glycerophosphoric acid (Ba salt). The radioactivity of the final acid is less if measured as Na salt in H_2O than if ashed before measurement.

R. S. C.

Determination of phosphoglyceric acid. O. MYERHOF and W. SCHULZ (Biochem. Z., 1938, 297, 60—65).— $[\alpha]_D^{20}$ of $d(-)$ -3-phosphoglyceric acid in neutral solution is approx. $+13.20^\circ$ but is changed to -745° by addition of excess of $\text{MoO}_4^{''}$. The concn. of the acid (< 0.05 mg. per c.c., e.g., in muscle extract deproteinised with $\text{CCl}_3\text{CO}_2\text{H}$ and neutralised) is determined by measuring the rotation before and after the addition of $\text{MoO}_4^{''}$, the difference corresponding with the amount of acid present. Interference due to inorg. $\text{PO}_4^{'''}$, excess of $\text{MoO}_4^{''}$, and other factors is compensated by making a blank determination. Interference by other substances (e.g., malic or tartaric acid, excess of lactic acid) is avoided by pptg. the phosphoglyceric acid with $\text{Pb}(\text{OAc})_2$ and decomp. the ppt. with dil. H_2SO_4 . The rotation of phosphoric esters without CO_2H (e.g., α -glycerophosphoric, hexose-mono- and -di-phosphoric acid), $d(+)$ -2-phosphoglyceric acid, and free sugars is only slightly or not at all affected by $\text{MoO}_4^{''}$. The equilibrium 3-phosphoglyceric acid \rightleftharpoons 2-phosphoglyceric acid is only slightly affected by temp. change between 0° and 60° .

W. McC.

Simple and nearly quantitative conversion of β - into α -glycerophosphates. (MILLER) M. C. BAILLY (Compt. rend., 1938, 206, 1902—1904; cf. A., 1934, 1331).—Na β -glycerophosphate with boiling 10% aq. H_2SO_4 or HCl is converted into the α -glycerophosphate (93% yield) which reduces HIO_4 (cf. A., 1933, 696) and can be isolated as the Na derivative.

J. L. D.

Synthetic phosphatide acids. II. Preparation of monofatty-acylated glycerophosphoric acids. H. ARNOLD (Ber., 1938, 71, [B], 1505—1510; cf. A., 1937, II, 365).—The products obtained by the action of chaulmoogric acid on α - or β -glycerophosphoric acid, or $\alpha\beta$ - or $\alpha\gamma$ -glycerodiphosphoric acid or their Na salts in presence of excess of conc. H_3PO_4 or by phosphorylation of the mono- or di-fatty acid esters of glycerol with P_2O_5 have little uniformity. The following compounds are obtained by the action of the requisite acid chloride on a suspension of the anhyd. Na glycerophosphate in dry C_6H_6 containing $\text{C}_6\text{H}_5\text{N}$: Na *hydno*carpoyl- β -glycerophosphate and the corresponding Pb salt, decomp. $> 300^\circ$; Na *chaulmoogroyl*- α -glycerophosphate, decomp. $> 200^\circ$, and the Pb salt, decomp. 190 — 200° ; Na *mono-oleoyl*- β -glycerophosphate, m.p. 180 — 185° after softening at 150° , and the Pb salt; Na *monostearoyl*- β -glycerophosphate, m.p. 165 — 170° , and the Pb salt. $\alpha\gamma$ -Dichaulmoogrin is obtained from Na chaulmoograte suspended in xylene and $\text{OH}\cdot\text{CH}(\text{CH}_2\text{Br})_2$ at 125° .

H. W.

Esters of orthosilicic acid. M. N. KALININ (Compt. rend. Acad. Sci. U.R.S.S., 1938, 18, 433—434).—The use of C_6H_6 as solvent in the interaction of SiCl_4 and ROH increases the yield of esters $\text{Si}(\text{OR})_4$,

where R = Me, Et, Bu^a , Bu^b , isoamyl. The prep. of $\text{SiCl}(\text{OEt})_3$ is similarly facilitated.

A. T. P.

Electrolysis of magnesium methyl iodide in pyridine solution. C. E. THURSTON and K. A. KOBE (Philippine J. Sci., 1938, 65, 139—142).—Using a divided cell and a Pt cathode, I is liberated at the anode and a brown powder (containing Mg and $\text{C}_5\text{H}_5\text{N}$) formed at the cathode with a small amount of unidentified gas.

E. S. H.

New method of resolving a racemic compound. G. KARAGUNIS and G. COUMOULOS (Nature, 1938, 142, 162—163; cf. A., 1938, II, 286).—Selective adsorption by powdered d - or l -quartz crystals in a Tswett column effects a partial resolution of $\{(\text{Cr en}_3)\text{Cl}_3 + 3\cdot 5\text{H}_2\text{O}\}$. Using d -quartz, activated by heating, the first elutions are dextro- and the next laevo-rotatory and vice versa.

L. S. T.

Lead alkyl compounds. G. CALINGAERT and H. SOROOS (J. Org. Chem., 1938, 2, 535—539).— PbMe_4 and I in Et_2O at -60° give 60% of Pb *trimethyl iodide*, which with $\text{CHMeEt}\cdot\text{MgBr}$ gives 50% of Pb *trimethyl sec-butyl*, b.p. $59/13$ mm., 16% of PbMe_4 , and 22% of $\text{PbMe}_2(\text{CHMeEt})_2$. PbMe_3Br gives a poorer yield of PbMe_3 derivative. PbMe_3Br and MgBu^tCl give PbMe_4 and Pb with some C_2Me_6 and (?) $\text{CH}_2\text{Pr}^b\text{Bu}^t$, but PbMe_3I gives 88% of Pb *trimethyl tert-butyl*, m.p. $5\cdot 7^\circ$, b.p. 47 — $47\cdot 2/13$ mm. PbCl_2 and MgMeI at -5° to -8° give 61% of Pb *hexamethyl*, m.p. 37 — 38° , obtained in only 7% yield from PbMe_3I and Na in NH_3 . The unexpected stability and crystal symmetry of PbMe_3Bu^t and Pb_2Me_6 are ascribed to their formal resemblance to C_2Me_6 .

R. S. C.

Organic osmium compounds. R. CRIEGEE (Angew. Chem., 1938, 51, 519—520).—A lecture.

C. R. H.

1:2-Dimethyl- Δ^1 - and - Δ^5 -cyclopentene and *cis*- and *trans*-1:2-dimethylcyclopentane. G. CHURDOGLU (Bull. Soc. chim. Belg., 1938, 47, 363—381).—Dehydration of 1:2-dimethylcyclopentanol by 80.3% HCO_2H gives a mixture of 1:2-dimethyl- Δ^1 -cyclopentene (I), b.p. $105\cdot 03/700$ mm., m.p. $-91\cdot 3^\circ$, and 1:2-dimethyl- Δ^5 -cyclopentene (II), b.p. $95\cdot 48$ — $95\cdot 50/760$ mm., m.p. $-118\cdot 1^\circ$ (other consts. recorded). The constitution of (I) follows from its oxidation by KMnO_4 to δ -ketohehoic acid (semicarbazone, m.p. 178°) and heptane- $\beta\zeta$ -dione, b.p. 96 — $97/11$ mm., m.p. about -30° (semicarbazone, decomp. 217° ; oxime, m.p. 86°), whilst that of (II) is deduced from its oxidation to δ -keto- γ -methyl- n -hexoic acid, b.p. 164 — $168/22$ mm. (semicarbazone, decomp. $163\cdot 5^\circ$ or m.p. 158° after softening at 153° when slowly heated). The acid is best obtained synthetically thus: $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et} \rightarrow \text{CHMeAc}\cdot\text{CO}_2\text{Et}$, $\text{CO}_2\text{Et}\cdot\text{CMeAc}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \rightarrow \text{CHMeAc}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. Hydrogenation (Pt-black in AcOH at room temp.) gives *trans*-, b.p. $91\cdot 78/760$ mm., m.p. -119° , and *cis*-, b.p. $99\cdot 23/760$ mm., m.p. $-52\cdot 5^\circ$, -1:2-dimethylcyclopentane, the configurations of which are decided by their physical properties.

H. W.

Supposed isomeric forms of methylcyclohexane. J. P. WIBAUT, S. L. LANGEDIJK, J. SMIT-

TENBERG, and H. HOOG (Chem. and Ind., 1938, 753).—The properties of pure methylcyclohexane (from PhMe) do not confirm Vogel's observations (A., 1938, II, 268). A. LI.

Multiplanar forms of methylcyclohexane. A. I. VOGEL (Chem. and Ind., 1938, 772—773).—The work of Wibaut *et al.* (preceding abstract) is considered to confirm the author's observations by an entirely independent method. H. W.

Kinetics of aromatic nitration in nitromethane solution.—See A., 1938, I, 404.

Synthesis and hydrogenation of polyalkylated benzenes. H. KOCH and H. STEINBRINK (Brennstoff.-Chem., 1938, 19, 277—285).— C_6Et_6 is not formed by the action of 96% H_2SO_4 and C_2H_4 on C_6H_6 and is produced only in very slight amount if Ag_2SO_4 and $NiSO_4$ are added to the acid; it is formed in 56—59% yield from C_6H_6 , $AlCl_3$, and C_2H_4 under pressure. Hydrogenation ($Ni-Mn-Al-SiO_2$ at 235—240° in cyclohexane) gives a mixture of the stereoisomeric hexaethylcyclohexanes (I) which has the properties of a spindle oil. Attempted further ethylation of (I) by $EtCl-AlCl_3$ or by $BF_3-C_2H_4$ in presence of $Ni-SiO_2$ gave inconclusive results. $C_6H_5Pr^B$, m.p. 118.5°, is not further alkylated by C_3H_6 and 96% H_2SO_4 in cyclohexane or by $BF_3-C_3H_6$ under pressure. With $AlCl_3$ and $AcCl$ it affords a triisopropylacetophenone, m.p. 105.6—106°, which does not react with $NH_2\cdot CO\cdot NH\cdot NH_2$. C_6Et_6 does not suffer similar alkyl replacement when treated with $AlCl_3$ and $AcCl$. Hydrogenation ($Ni-Al-Mn-SiO_2$ in cyclohexane) of $C_6H_5Pr^B$ gives the stereoisomeric tetraisopropylcyclohexanes, m.p. 125.2—125.8° and b.p. 150—153°/20 mm., each of which behaves as a spindle oil. The viscosity and ageing properties of C_6Et_6 , $C_6H_5Et_5$, $C_6H_5Pr^B$, and $C_6H_5Pr^B$ are recorded. Exhaustive treatment of C_6H_6 and 96% H_2SO_4 with isobutene leads essentially to *p*-ditert-butylbenzene, a large proportion of the gas being polymerised. $AcCl$ and $AlCl_3$ in CS_2 transform it into tert-butylacetophenone [semicarbazone, m.p. 225—227° (decomp.)]. It is hydrogenated ($Ni-Mn-Al-SiO_2$ in cyclohexane) to a difficultly separable mixture of the stereoisomeric *p*-ditert-butylcyclohexanes, one of which has m.p. 94.5—95°. The alkylation of C_6H_6 with Δ^4 -butene, a pentene, and a decene fraction and of Ph_2 with C_2H_4 did not give homogeneous products. The products of the action of C_6H_6 on Pr^aCl , Bu^aCl , and *n*-amyl chloride in presence of $AlCl_3$ or H_2SO_4 are described. H. W.

Accessory products [formed during chlorination of toluene].—See A., 1938, I, 408.

Action of aluminium chloride on fluorinated compounds. A. L. HENNE and M. S. NEWMAN (J. Amer. Chem. Soc., 1938, 60, 1697—1698).— $CPhF_3$, $AcCl$, and $AlCl_3$ give AlF_3 and $CPhCl_3$ in excellent yield; in the absence of $AcCl$ much tar is formed, indicating participation of the $AcCl-AlCl_3$ complex in the reaction. Org. fluorides, $AlCl_3$, and ethylenes gives tars. In C_6H_6 (CCl_2F) $_2$, $CCl_2F\cdot CClF_2$, ($CClF_2$) $_2$, $CHClF_2$, and $C_2Cl_2F_2$ give HCl , a little HF , AlF_3 , and F-free, rubbery, polymerised substances. $CCl_2F\cdot CClF_2$ and $AlCl_3$ (no C_6H_6) give AlF_3 and a

little $CCl_3\cdot CClF_2$ and higher-boiling, F-free material. $CHCl_2\cdot CClF_2$ reacts more readily, giving HF , tars, and AlF_3 . Thus, $AlCl_3$ cannot be used for Friedel-Crafts reactions with fluorides. R. S. C.

Nitration of phenylnitromethane, and a new isomeride of trinitrotoluene. T. URBANSKI and J. GIEDROYĆ (Rocz. Chem., 1938, 18, 125—130).— $CH_2Ph\cdot NO_2$ and 80% NHO_3 at 35—40° yield *m*- $NO_2\cdot C_6H_4\cdot CH_2\cdot NO_2$, which with 1:1 HNO_3 —20% oleum at >65° gives 3:5-dinitrophenylnitromethane, m.p. 130°; this is more readily detonated by shock, and less so by heat, than is $C_6H_2Me(NO_2)_3$ (I), although thermal decomp. begins at a lower temp. (200°). Its explosive power is equal to that of (I). R. T.

Prototropy of the nitromethanes. I. Chloro-, bromo-, and nitro-phenylnitromethanes. R. G. COOKE and A. K. MACBETH (J.C.S., 1938, 1024—1026).—The rate of the change, $C_6H_4R\cdot CH\cdot NO\cdot O^- + H^+ \rightarrow C_6H_4R\cdot CH_2\cdot NO_2$, in 50% aq. $EtOH$ at 0° is measured for substances in which $R = o$ -, *m*-, and *p*- NO_2 -, $-Br$, and $-Cl$. In all cases, except that of *o*- NO_2 (where an *o*-effect is observed), the reaction mechanism is probably the same, as the graphs show first a curved and then a straight portion. The relative rates are $NO_2 > Hal > H$, and, for NO_2 only, $p > m$. The following are new: *o*-, b.p. 109°/10 mm., and *m*-, b.p. 128°/13 mm., m.p. 23°, -chloro-, *o*-, an oil, b.p. 139°/7 mm. (lit., m.p. 55—56°), and *m*-bromophenylnitromethane, m.p. 23—24°. R. S. C.

Stabilising action of quinol on the thermal polymerisation of styrene. J. W. BREITENBACH, A. SPRINGER, and K. HOREISCHY (Ber., 1938, 71, [B], 1438—1441).—The polymerisation of styrene (I) by heat is almost entirely inhibited by quinol (II) in presence of O_2 . A marked induction period is caused by O_2 . Since at the beginning the rate is the same in the presence or absence of O_2 it appears that an additive compound first results from (I) and O_2 which then by decomp. or union with a further mol. of (I) gives a polymerisation nucleus. The stabilising effect of (II) is due to its reducing power. The similar influence of *p*-benzoquinone (III) on reaction and sp. viscosity of polymerisates show that its influence lies in increasing the rupture of the chain; it is consumed by the reaction, either being involved by the polystyrene or reduced to (II). During the course of the change the intensity of the colour in presence of (III) decreases gradually. H. W.

Cumulenes. II. Improved method of preparation. R. KUHN and K. WALLENFELS (Ber., 1938, 71, [B], 1510—1512; cf. A., 1938, II, 226).—Treatment of diacetylenic glycols in Et_2O containing HCl with reducing agents (VCl_2 , $CrCl_2$) gives cumulenes in excellent yield. Metals are unsuitable. The prep. of tetraphenyl- and didiphenylene-hexapentaene is described. H. W.

Catalytic hydrogenation in the naphthalene series. L. PALFRAY (Compt. rend., 1938, 206, 1976—1978).— $\alpha-C_{10}H_7\cdot OH$ with H_2 (150 kg. pressure)—Raney Ni at 65° rapidly affords 1-hydroxy-1:2:3:4-tetrahydronaphthalene and tetrahydronaphthalene, which when further reduced (many hr.) afford 1-decahydronaphthol and decahydronaphthal-

one, respectively. Similarly, β - $C_{10}H_7\cdot OH$ at 65° affords mainly 2-hydroxy-1:2:3:4-tetrahydronaphthalene (I) and a little decahydronaphthol. Further reduction of (I) at 125° affords a mixture of *cis*- and *trans*-2-decahydronaphthol from which the former is isolated. Similarly, $C_{10}H_8$ at 100° affords $C_{10}H_{12}$ which at 200° gives $C_{10}H_{18}$. J. L. D.

Dehydrogenation. I. S. C. SENGUPTA (J. pr. Chem., 1938, [ii], 151, 82—96).—Addition of $AlCl_3$ to α -dimethylsuccinic anhydride in C_6H_6 gives β -benzoyl- α -dimethylpropionic acid (I), m.p. $170—171^\circ$ (semicarbazone, m.p. 166°), the *Me* ester, m.p. 50° , of which is obtained by the successive action of $SOCl_2$ and $AlCl_3$ on the compound $COCl\cdot CMe_2\cdot CH_2\cdot CO_2Me$. $Zn-Hg$ and conc. HCl reduce (I) to γ -phenyl- α -dimethylbutyric acid, b.p. $155—156^\circ/6$ mm., m.p. 98° (anilide, m.p. $113—114^\circ$), the *Et* ester, b.p. $114^\circ/5$ mm., of which could not be condensed with $Et_2C_2O_4$. The acid is cyclised by H_2SO_4 at 100° to 1-keto-2:2-dimethyl-1:2:3:4-tetrahydronaphthalene, b.p. $150^\circ/27$ mm. (oxime, m.p. $131—132^\circ$), which does not give a semicarbazone or phenylhydrazine; this is oxidised by $KMnO_4-KOH$ to o - $C_6H_4(CO)_2O$ and reduced (Clemmensen) to 2:2-dimethyl-1:2:3:4-tetrahydronaphthalene, b.p. $123^\circ/34$ mm., which could not be dehydrogenated by Se at $280—340^\circ$ in an open vessel but passes in a sealed tube at $300—320^\circ$ into 2- $C_{10}H_7Me$. Similarly, β -*p*-toluoyl- α -dimethylpropionic acid, m.p. $158—159^\circ$ (semicarbazone, m.p. $166—167^\circ$; *Me* ester, b.p. $150^\circ/7$ mm.), gives successively γ -*p*-tolyl- α -dimethylbutyric acid, m.p. $111—112^\circ$ (anilide, m.p. 119° ; *Et* ester, b.p. $120—121^\circ/5$ mm.), 1-keto-2:2:7-trimethyl-1:2:3:4-tetrahydronaphthalene, b.p. $120—121^\circ/5$ mm. (oxime, m.p. $141—142^\circ$), 2:2:7-trimethyl-1:2:3:4-tetrahydronaphthalene, b.p. $128^\circ/23$ mm., and 2:7- $C_{10}H_6Me_2$. β -Benzoyl- α -diethylpropionic acid, m.p. $91—92^\circ$ (semicarbazone, m.p. 114° ; *Me* ester, b.p. $160—162^\circ/8$ mm.), gives γ -phenyl- α -diethylbutyric acid, b.p. $185—186^\circ/5$ mm., m.p. $49—50^\circ$ (anilide, m.p. $114—115^\circ$; *Et* ester, b.p. $95—96^\circ/6$ mm.), α -keto-2:2-diethyl-1:2:3:4-tetrahydronaphthalene, b.p. $148—150^\circ/7$ mm., 2:2-diethyl-1:2:3:4-tetrahydronaphthalene, b.p. $110^\circ/4$ mm., and 2- $C_{10}H_7Et$. H. W.

Chlorination of 2-methylnaphthalene. O. ACHMATOWICZ and K. LINDENFELD (Rocz. Chem., 1938, 18, 69—74).—The following substances were isolated from the complex mixture resulting from chlorination of 2- $C_{10}H_7Me$ at 220° , in diffused light: 1-chloro-2-methylnaphthalene (I), b.p. $162—164^\circ/30$ mm. [identical with Scherler's *eso*-chloro- β -methylnaphthalene (A., 1892, 493), 2- $C_{10}H_7\cdot CH_2Cl$, 1-chloro-2-chloromethylnaphthalene (II), m.p. $78—79^\circ$, and 2-dichloromethylnaphthalene (III), m.p. $114—115^\circ$. (I) is chlorinated at 225° , to yield (II), which gives with boiling aq. $Pb(NO_3)_2$ 1-chloro-2-hydroxymethylnaphthalene, m.p. $98—99^\circ$ (benzoate, m.p. $68—69^\circ$), and this is oxidised ($KMnO_4$) to 1:2- $C_{10}H_6Cl\cdot CO_2H$ (*Me* ester, m.p. 50°). (III) and H_2O at $140—150^\circ$ (8 hr.) yield β - $C_{10}H_7\cdot CHO$. R. T.

Hydrocarbons and hydrocarbon intermediates of high mol. wt. L. A. MIKESKA, C. F. SMITH, and E. LIEBER (J. Org. Chem., 1938, 2, 499—505).—

Passing HCl into a boiling mixture of stearophenone (I) (modified prep.), m.p. $63.5—64.5^\circ$, mossy $Zn-Hg$, xylene; and conc. HCl gives a good yield of $Ph\cdot C_{16}H_{33}\cdot n$ (II); other methods were less successful. H_2-PtO_2 reduces (II) in $AcOH$ to *n*-octadecylcyclohexane, m.p. 40° , b.p. $204—210^\circ/4$ mm. $MgBu^uCl$ and (I) give phenyl-*n*-butyl-*n*-heptadecylcarbinol, b.p. $235—240^\circ/2$ mm., dehydrated by $H_2C_2O_4$ at $180—200^\circ$ in CO_2 to α -*n*-butyl-*n*- Δ^a -octadecenylbenzene, b.p. $205—210^\circ/1$ mm.; which is hydrogenated (PtO_2) in $AcOH$ to α -*n*-butyl-*n*-octadecylbenzene, m.p. 38° , b.p. $200—201^\circ/1$ mm. Adding $AlCl_3$ to stearyl chloride (modified prep.) and Ph_2 in CS_2 gives stearyldiphenyl, m.p. $106—107^\circ$, reduced to *n*-octadecyldiphenyl, m.p. $79—81^\circ$, b.p. $270—275^\circ/5$ mm., and converted by $MgBu^uCl$ etc. into α -*n*-butyl-*n*- Δ^a -octadecenylidiphenyl; α -*n*-butyl-*n*-octadecyldiphenyl, m.p. $41.5—43^\circ$, and 1-cyclohexyl- α -*n*-butyl-*n*-octadecylcyclohexane, b.p. $255—260^\circ/1$ mm. Similar reactions afford 1-stearyl-, m.p. $54.5—56^\circ$, 1- α -*n*-butyl-*n*- Δ^a -octadecenyl-, b.p. $232—240^\circ/3$ mm., and 1- α -*n*-butyl-*n*-octadecyl-naphthalene, m.p. 38° , b.p. $200—201^\circ/2$ mm., stearyl-, m.p. $49.5—50^\circ$, *n*-octadecyl- (III), an oil, α -*n*-butyl-*n*- Δ^a -octadecenyl-, b.p. $263—264^\circ/4$ mm., and α -*n*-butyl-*n*-octadecyl-tetrahydronaphthalene (IV), b.p. $235—245^\circ/2$ mm., and other products previously reported (B., 1936, 1077). Hydrogenation of (III) and (IV) yields *n*-octadecyl-, m.p. $43—47^\circ$, and α -*n*-butyl-*n*-octadecyl-octahydronaphthalene, b.p. $240—245^\circ/3$ mm., respectively. R. S. C.

Synthesis of condensed polynuclear hydrocarbons by the cyclodehydration of aromatic alcohols. VII. Cyclodehydration involving the Wagner rearrangement. D. PRICE, D. DAVIDSON, and M. T. BOGERT (J. Org. Chem., 1938, 2, 540—545).—Cyclisation of $Ph\cdot [CH_2]_n\cdot CHBu^u\cdot OH$ ($n = 1$ or 2) by 90% H_2SO_4 involves a previous Wagner rearrangement. $CH_2Ph\cdot CH_2\cdot CHO$ and $MgBu^uCl$ in Et_2O at $2—10^\circ$ give 70% of ϵ -phenyl- $\beta\beta$ -dimethylpentan- γ -ol, b.p. $90—91^\circ/2$ mm. (phenylurethane, m.p. 91°), converted by 90% H_2SO_4 at 2° —room temp. into 1:1:2-trimethyl-1:2:3:4-tetrahydronaphthalene (55% yield), b.p. $77—77.5^\circ/1$ mm., $242^\circ/760$ mm., oxidised by $KMnO_4$ to o - $CO_2H\cdot C_6H_4\cdot CMe_2\cdot CO_2H$, dehydrogenated by S to 1:2- $C_{10}H_6Me_2$, and obtained in 86% yield by the action of 90% H_2SO_4 on ϵ -phenyl- $\beta\gamma$ -dimethylpentan- γ -ol, b.p. $118—119^\circ/3$ mm. (obtained in 50% yield from $CH_2Ph\cdot CH_2\cdot MgBr$ and $COMePr^a$). $CH_2Ph\cdot CHO$ and $MgBu^uCl$ give α -phenyl- $\gamma\gamma$ -dimethylbutan- β -ol, b.p. $78.5^\circ/2$ mm., converted by H_2SO_4 at $<5^\circ$ into 1:1:2-trimethylindane (41%), b.p. $208^\circ/760$ mm., oxidised by CrO_3-AcOH to *Me* β -*o*-carboxyphenylisopropyl ketone, m.p. 157.5° (corr.). R. S. C.

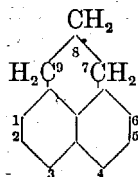
Comparison of three meso-anthracenic additive reactions; diene synthesis, photo-oxidation, and hydrogenation. C. DUFRASSE, L. VELLUZ, and (MME.) L. VELLUZ (Bull. Soc. chim., 1938, [v], 5, 1073—1081).—A comparison of the conditions under which the maleic additive compounds and the photo-oxides of anthracene are produced and dissociate shows that the analogies noted previously are merely superficial and fortuitous and are limited without doubt to the meso-anthracenic structure.

Comparison with the hydrides establishes the importance of the bridge position for the dissociability of a *meso*-anthracene additive product. 9:10-Dihydroanthracene cannot be photo-oxidised. This is also true of 9-phenyl-9:10-dihydroanthracene, whilst 9:10-diphenyl-9:10-dihydroanthracene is very stable towards heat and light and, in particular, is not photo-oxidisable. endo-9:10- α -Anhydroadicarboxyethylene-, m.p. 267° (block), -9-phenyl-, m.p. 290—291° (block), and -9:10-diphenyl-, m.p. 315—317° (block), -9:10-dihydroanthracene are obtained in the usual manner; the last-named is decomposed most easily and most completely into its components by heat.

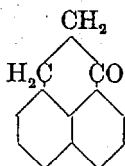
H. W.

Factors affecting the addition of bromine to phenanthrene. M. S. KHARASCH, P. C. WHITE, and F. R. MAYO (J. Org. Chem., 1938, 2, 574—576).—Addition of Br to phenanthrene is catalysed by intermittent, almost as much as by continuous, illumination, reaction being faster in air than in vac. Thus, Price measured a catalysed reaction (A., 1936, 1498; 1937, II, 12). Bz₂O₂ accelerates the reaction in the dark, but less so than does ascaridole (I). (I) is more effective with a low than with a high [Br]. R. S. C.

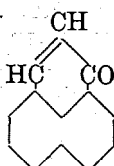
Synthesis of 3:4-benzpyrene derivatives. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1938, 60, 1658—1665).—The names, perinaphthane, perinaphthan-7-one, and perinaphthenone, for (I), (II), and (III), respectively, are preferred as being more systematic than those hitherto proposed. Convenient syntheses of substances in this and the benzpyrene series are described. Ring-closure of



(I.)



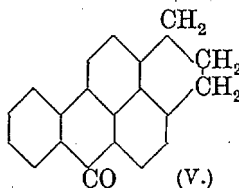
(II.)



(III.)

1-allylnaphthalene (prep. in 81% yield from 1-C₁₀H₇Br, Mg, and CH₂:CH:CH₂Br), b.p. 127.5—128.5°/8 mm. (*picrate*, m.p. 68—69°), could not be effected; distillation at 500—550°/15 mm. over activated Al₂O₃ gives 1-propenylnaphthalene, b.p. 139—140°/10 mm. (*picrate*, m.p. 110—111°; oxidised by K₂Cr₂O₇ to MeCHO and α -C₁₀H₇·CO₂H). β -C₁₀H₇·OH and glycerol are condensed and oxidised by NO₂·C₆H₄·SO₃Na in H₂SO₄ to (III) (26% yield), m.p. 156—156.5°, hydrogenated by H₂-Cu-Cr₂O₃ in dioxan or Et₂O, best at 250—260°/120 atm., to (I) (74% yield), m.p. 65.1—65.4° [*picrate*, m.p. 150—151°; C₆H₃(NO₂)₃ additive compound, m.p. 160—161°], with a little perinaphthan-7-ol (IV), m.p. 105.5—106° (*picrate*, m.p. 163.5—164.5°). (IV) is the main product (49%) obtained by means of H₂-Raney Ni in dry Et₂O-EtOH. H₂-PtO₂ in dry EtOH converts (III) into an unstable, bimol. product, C₂₆H₁₈₋₂₀O₂, m.p. 179—180° (decomp.). With the complex from AlCl₃ and BzCl in CS₂ (I) gives 3-benzoylperinaphthane (95% yield), m.p. 62—63°, b.p. 210—215°/2 mm., converted by NaCl-AlCl₃ in O₂ at 150—155° into 2:1'-trimethylene-1:9-benzanthr-10-one (V) (26% yield), m.p. 217—218°, which, when distilled with Zn

dust at 1—2 atm., gives 3:4-benzpyrene (VI), m.p. 178.5—179° [best purified by way of the C₆H₃(NO₂)₃ additive compound, m.p. 226—227°]; the mother-liquor from (V) contains some further reduced benzanthrone derivative, converted into (VI) by Zn distillation, and a 50% yield of (VI) is

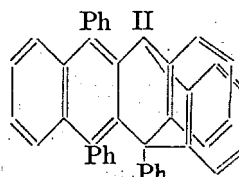


(V.)

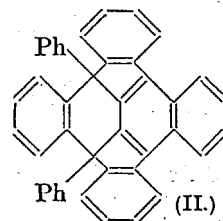
obtained if isolation of (V) is omitted. The appropriate C₆H₄Me·COCl, (I), and AlCl₃ in CS₂ yield 3-o- (VII), m.p. 68—69°, b.p. 210—220°/0.2 mm., 3-m- (VIII), m.p. 86.5—87°, b.p. 225—230°/2 mm., and 3-p-toluylperinaphthane (IX), m.p. 90—90.5°, b.p. 215—220°/0.5 mm. Ring-closure of (IX) gives 2'-methyl-3:4-benzpyrene (42% yield), m.p. 138—139° (after resolidification, 140—140.2°) [C₆H₃(NO₂)₃ additive compound, m.p. 211.5—212°; *picrate*, m.p. 184—185°]. (VII) and (VIII) give 22 and 14%, respectively, of 3'-methyl-3:4-benzpyrene, m.p. 146.5—147° (after resolidification, 147.6—148.1°) [C₆H₃(NO₂)₃ additive compound, m.p. 210.5—211°; *picrate*, m.p. 179.5—180°]. The rearrangement involved in the ring-closure of (VII) is discussed. Pure 1':2':3':4'-tetrahydro-3:4-benzpyrene has m.p. 112.6—113.1° (cf. Fieser and Fieser, A., 1935, 741; Winterstein *et al.*, *ibid.*, 968). High-pressure hydrogenation thereof gives a mixture (cf. *loc. cit.*). M.p. are corr.

R. S. C.

Dissociability of organic oxides. Transformations of tetra-arylnaphthacenes and their oxides. M. ENDERLIN (Ann. Chim., 1938, [xi], 10, 5—116).—10:12-Diphenyl-9:11-di-p-tolynaphthacene is converted by H₂SO₄ or HI into ψ -diphenyldi-p-tolynaphthacene, form I, m.p. 294—295°, isomeride II, m.p. 271—272°. Analogously ψ -diphenyldi-p-bromophenylnaphthacene exists in two modifications, m.p. 345° (block) and 295°, respectively. The existence of these compounds in two isomeric forms, their



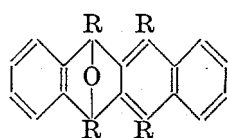
(I.)



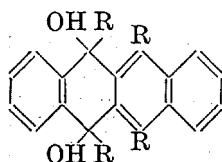
(II.)

analogy to C₂Ph₆, and the occurrence of a single Ph₄ compound is best explained by the formulation (I). Dehydration of the requisite mono- or di-hydroxides affords 9:10-diphenyl-9:12:10:11-diphenylene-9:10-dihydronaphthacene (II), m.p. 430° (block), phenyl-p-tolylphenylenemethylphenylenenaphthacene, m.p. about 370°, and phenyl-p-bromophenylphenylenebromophenylenenaphthacene, m.p. 450° (block), respectively. The naphthacenes are converted into their monoxides by oxidation with dil. HNO₃, KMnO₄, or CrO₃, by reduction of the higher oxides by Zn and AcOH, and by dehydration of the requisite (OH)₂-compounds. They are stable to air and light, are not decomposed by heat, are readily reduced to the corresponding hydrocarbons, cannot be oxidised to the higher oxides, and do not react with Grignard reagents. 10:12-Diphenyl-9:11-di-p-tolynaphthacene oxide, m.p. 265° or

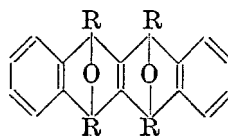
(+C₆H₅) m.p. 175°, and 10:12-diphenyl-9:11-di-p-bromophenylnaphthacene oxide, m.p. 274—276°, or (+C₆H₅), m.p. about 220°, are new. Dihydroxydihydrodiphenyl-naphthacenes are obtained by the action of Grignard's reagents, particularly MgEtBr, on the dissociable oxides but the method does not invariably lead to homogeneous products and oxidation of the hydrocarbons by KMnO₄ is preferable. They are colourless compounds with 2 active H (Zerevitinov); they do not dissociate when heated but lose H₂O at a moderate temp. with production of the monoxide. Further dehydration yields the diaryldiarylenenaphthacenes. They are readily reduced to the hydrocarbons. Dihydroxy-9:10:11:12-tetraphenyldihydronaphthacene, which when heated loses successively solvent and H₂O of crystallisation, dihydroxy-10:12-diphenyl-9:11-di-p-tolyldihydronaphthacene, m.p. 210—220° according to the mode of heating, and dihydroxy-10:12-diphenyl-9:11-di-p-bromophenyldihydronaphthacene, m.p. 220—230° (block; decomp.), are described. The dissociable oxides are transformed into the iso-oxides by Grignard's reagents or, more simply, by Mg salts; usually the products are difficultly separable mixtures. The iso-oxides are colourless compounds which do not dissociate into O and hydrocarbon. Reduction leads to the hydrocarbon in poor yield and sometimes causes elimination of Ph. It appears impossible to transform them into a lower oxide or a diaryldiarylenenaphthacene. Tetraphenylnaphthacene isooxide, m.p. 169—168° and 267—268°, diphenyldi-p-tolylnaphthacene isooxide, m.p. 210° (block), and diphenyldi-p-bromophenylnaphthacene isooxide, m.p. 258° (block), have been obtained.



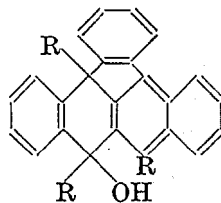
(III.)



(IV.)



(V.)



(VI.)

Tetraphenylnaphthacene peroxide is converted by 50% H₂SO₄ in C₆H₆ into tetraphenylnaphthacene ψ -oxide, C₄₂H₂₈O₂, decomp. 210° (block), which when solid or dissolved is rapidly transformed by light into a yellow resin. It readily liberates I from acidified KI, reacts vigorously with Grignard reagents (= 1 H), and is reduced by Zn and dil. AcOH to diphenyldiarylenenaphthacene. The constitutions (III), (IV), (V), and (VI) are advanced for the monoxides, dihydroxides, isooxides, and ψ -oxides, respectively. Support of these conclusions is found in the thermochemical behaviour of the hydrocarbons and their intermediate oxides and in their magnetic properties.

H. W.

Catalytic hydrogenation of quaternary ammonium salts. O. ACHMATOWICZ and K. LINDENFELD (Rocz. Chem., 1938, 18, 75—87).—Catalytic hydrogenation (C-Pd catalyst) of quaternary NH₄ salts proceeds as follows, at 20 and 85°: NMe₃·RCl \rightarrow NMe₃ + RH + HCl, in the cases R = allyl, Ph, [CH₂]_n·Ph (n = 1—4), and CHPh·CH·CH₂. NMe₂Cl(CH₂Ph)₂ yields PhMe, HCl, and NMe₂·CH₂Ph (further hydrogenated to PhMe and NHMe₂). The following new compounds were obtained incidentally, by the standard method: δ -phenylbutyl- (aurichloride, m.p. 149—150°), and 2-naphthylmethyl-trimethylammonium chloride (aurichloride, m.p. 188°; hydrogenation products, NMe₃, HCl, and a methyldihydronaphthalene, b.p. 226—228°).

R. T.

Catalytic oxidation of aromatic amines and phenols by means of clay and similar substances. A. EISENACK (Naturwiss., 1938, 26, 430).—Catalytic oxidation of the vapours of solid and liquid aromatic amines and phenols can be effected by the use of clay, fuller's earth, kaolin, flint, agate, pptd. Al and Mg silicates, permutit, SiO₂ gel, etc. NPhMe₂ gives crystal-violet and its leuco-base and colour base, and NHPH₂ gives diphenylbenzidine and a deep blue quinonoid derivative.

A. J. M.

Organic catalysts. XIX. Esterase model. IV. W. LANGENBECK and K. HÖLSCHER (Ber., 1938, 71, [B], 1465—1471).—Further examples are cited of the ready hydrolysis of acylcarbinyl esters and glycolarylamides. The following appear new: acetoxycet- β -naphthylamide, m.p. 128°, 1-bromo-2-naphthylamide, m.p. 133°, 1-methoxy-2-naphthylamide, m.p. 125°, 3-methoxy-2-naphthylamide, m.p. 134°, 6-methoxy-2-naphthylamide, m.p. 147—148°, and 7-methoxy-2-naphthylamide, m.p. 134°; 9-, 2-, and 3-phenanthroylcarbinyl acetate, m.p. 122—123°, 117°, and 116—117°, respectively; 9- and 3-phenanthrolyldiazomethane, m.p. 120° and 130—133° (decomp.), respectively. Reply is made to Ionescu and Cotani (A., 1938, III, 695).

H. W.

New radical with quadrivalent nitrogen; phenyl-9-trans-decahydronaphthyl nitrogen oxide. W. HÜCKEL and W. LIEGEL (Ber., 1938, 71, [B], 1442—1445).—9-Nitroso-trans-decahydronaphthalene (I) does not form azo- or azoxy-compounds with NH₂Ph, cyclohexylamine, or NHPH·OH. It is converted smoothly by MgPhBr into phenyl-trans-9-decahydronaphthylhydroxylamine (II), m.p. 141—143° (decomp.) (Ac, m.p. 87°, Bz, m.p. 133°, and p-nitrobenzoyl, m.p. 142—143°, derivatives), which is reduced by Na and abs. EtOH or by H₂-Pd-CaCO₃ in EtOH to phenyl-trans-9-decahydronaphthylamine (III), m.p. 81°. This is transformed by NaNO₂ and conc. HCl into p-nitrosophenyl-trans-9-decahydronaphthylamine, m.p. 159°, hydrogenated, and then acetylated to the compound, C₁₈H₂₆ON₂, m.p. 212—213°. The mother-liquors from (II) contain phenyl-trans-9-decahydronaphthyl nitrogen oxide Ph·N(:O)·C₁₀H₁₇, m.p. 83°, also obtained by autoxidation of (II) in C₆H₆; it is reduced (H₂-Pd-CaCO₃ in EtOH) to (III). MgMeI, Mg cyclohexyl chloride, and MgBuⁿBr essentially reduce (I) to (II).

H. W.

Manufacture of substituted phenylcarbimides.—See B., 1938, 888.

Carbodiarylimides. F. ZETZSCHE, H. E. MEYER, H. OVERBECK, and W. NERGER (Ber., 1938, 71, [B], 1512—1516).—The desulphurisation of thiocarbamides to carbodiarylimides (I) is best effected by PbO in boiling PhMe, volatilisation of the H₂O diminishing the tendency towards the production of carbamides. The tendency of (I) towards polymerisation varies greatly, being most pronounced with the *p*-iodophenyl and least with the pyridyl derivative. The use of surface catalysts should be avoided. The following are described: carbodi-*p*-tolylimide, b.p. 202°/12 mm., m.p. 56°, readily converted by boiling H₂O, steam, or dil. H₂O₂ into the resinous form; carbodi-*p*-bromo-, b.p. 231—234°/12 mm., 188°/0.2 mm., m.p. 70—73°, and -*iodo-phenylimide*, m.p. (crude) 90°, which decomposes at 180° and is transformed into different polymerides by crystallisation from various solvents; carbodi-2-pyridylimide, m.p. 137° (picrate, decomp. 228°); carbodi-*p*-dimethylaminophenylimide, m.p. 86—88.5°.

H. W.

Characterisation of carboxylic acids as ureides [acyldiarylcabamides] by means of carbodiimides. II. F. ZETZSCHE, H. E. MEYER, H. OVERBECK, and H. LINDLAR (Ber., 1938, 71, [B], 1516—1521).—BzOH does not react with carbodi-2-pyridylimide in boiling C₆H₆ or PhMe or in absence of solvent at 140°; at 180—200° 2-benzamidopyridine, m.p. 80° (picrate, m.p. 146°), is produced in 85% yield. The following 2-acyl-amidopyridines are obtained analogously: *sebac*-, m.p. 139° (picrate, m.p. 193°); *cinnam*-, m.p. 139° (picrate, m.p. 199°); *α-croton*-, m.p. 79° (picrate, m.p. 137°); *stear*-, m.p. 78° (picrate, m.p. 114°); *palmit*-, m.p. 69° (picrate, m.p. 108°); *ole*-, m.p. 15—18° (picrate, m.p. 68°); *linole*-, m.p. 57°. Carbodi-*p*-dimethylaminophenylimide appears superior to the compounds described previously (A., 1938, II, 257) since it does not polymerise when solid and is less easily anhydridised. With AcOH in COMe₂ at room temp. it slowly affords *aceti*-*p*-dimethylaminophenylcarbamide, m.p. 149°. The following acyl-di-*p*-dimethylaminophenylcarbamides are described: *propion*-, m.p. 162—163° after softening at 159°; *myrist*-, m.p. 120—120.5° after softening at 119° (picrate, m.p. 142—143°); *palmit*-, m.p. 120—122° after softening at 119° (picrate, m.p. 144—145°); *benz*-, m.p. 216—218° (picrate, m.p. 175°); *phellon*-, m.p. 160—163°; *p-azoxybenz*-, decomp. 292—298° (red at 190°); *lævul*-, m.p. 155°; *ole*-, m.p. 100—101° after softening at 98°; *linole*-, m.p. 88—89° (picrate, m.p. 129°); *linolen*-, m.p. 84—85°. The pyridines and carbamides are readily hydrolysed by conc. H₃PO₄ at 130—140° whereby CO(NH·C₆H₄·NMe₂) is degraded to *p*-NH₂·C₆H₄·NMe₂.

H. W.

Phenylthiocarbamides. The triad -N·C·S-. VI. Action of nitrous acid on *N*-phenyl-*N'*-methylthiocarbamide. VII. Some hydrolytic decompositions of phenylthiocarbamide. Action of sodium ethoxide on phenylthiocarbamide and of acetic anhydride and hydrolytic agents on *N*-phenyl-*N*- and -*N'*-methylthiocarbamide. K. B. LAL and H. KRAIL (J. Indian Chem. Soc., 1938, 15, 217—220, 221—228).—VI. NHPH·CS·NHMe with NaNO₂ in aq. EtOH-AcOH yields *N'*-nitroso-*N*-phenyl-*N'*-methylthiocarbamide,

m.p. 84° (decomp.). This with cold H₂O slowly yields NO, N₂, S, and PhNCS (the last slowly giving place to a non-basic solid, m.p. 137°), with cold NaOH yields PhNCS, and with warm dil. HCl gives NO, S, and a base (I), C₁₆H₁₃N₄S, m.p. 82°, which yields in EtOH a *picrate*, m.p. 195°, and in dil. HCl (usually) an isomeric *picrate*, m.p. 153—154°, and when heated gives PhNCS and a basic resinous substance. NaNO₂ in HCl partly oxidises NHPH·CS·NHMe to a base which deposits S, giving (I).

VII. The extent to which NHPH·CS·NH₂ is hydrolysed by NaOH, H₂O, and dil. HCl to NH₂Ph + HCNS, or to NH₃ + PhNCS, has been studied. Traces of COS are always produced. HCNS is determined either by pptg. with NiSO₄ and C₅H₅N and determining excess of Ni, or by Volhard's method after decomp. NHPH·CS·NH₂ with NH₃-AgNO₃, and PhNCS by steam-distilling and heating the distillate with NH₃-AgNO₃. NHPH·CS·NH₂ and NaOEt heated in EtOH yield some Na₂S, but when heated dry give chiefly NaCNS. With Ac₂O, HCl, H₂O, or NaOH, NHPH·CS·NH₂ yields (at varying rates) mainly NHPHMe + HCNS, whilst NHPH·CS·NHMe gives mainly NH₂Me + PhNCS.

A. LI.

Identification of prontosil album, *p*-aminobenzenesulphonamide. F. AMELINK (Pharm. Weekblad, 1938, 75, 851—853).—*p*-NH₂·C₆H₄·SO₂·NH₂ gives characteristic crystals with the following reagents (sensitivity given in parentheses): PtCl₄-HCl; PtCl₄-NaBr (0.2%); picric (0.5%) and picrolonic acids (0.5%); Br (0.1%) [also given by *p*-NH₂·C₆H₄·SO₃H (I)]. The pine-shaving reaction (orange-yellow decolorised by NH₃ vapour) differentiates it from (I).

S. C.

Microscopic identification of sulphanilamide. M. L. YAKOWITZ (J. Assoc. Off. Agric. Chem., 1938, 21, 351).—The condensation products of *p*-NH₂·C₆H₄·SO₂·NH₂ with PhCHO and cinnamon oil have characteristic cryst. forms, which are described.

E. C. S.

Microscopical identification of sulphanilamide.—See B., 1938, 977.

***p*-γ-Phenylpropylaminobenzenesulphonamide.**—See B., 1938, 981.

Derivatives of *p*-aminobenzenesulphonanilide. I. G. L. WEBSTER and L. D. POWERS (J. Amer. Chem. Soc., 1938, 60, 1553—1555).—*p*-NHAc·C₆H₄·SO₂Cl (I) and NO₂·C₆H₄·NH₂ in hot NPhMe₂ give *p*-acetamidobenzenesulphon-*o*-, m.p. 200—201°, -*m'*-, m.p. 236—237°, and -*p'*-nitroanilide, 237—238°, reduced by FeSO₄-NaOH to *p*-acetamidobenzenesulphon-*o*- (II), m.p. 222—223°, -*m'*- (III), m.p. 217—218°, and -*p'*-aminoanilide (IV), m.p. 232°. OH·C₆H₄·NH₂ and (I) in hot NPhMe₂ or, better, aq. NaOAc at 75° give *p*-acetamidobenzenesulphon-*o*-, m.p. 216—217°, -*m'*- (V), m.p. 217—218°, and -*p'*-hydroxyanilide, m.p. >260°. Hydrolysis by HCl-EtOH affords *p*-aminobenzenesulphon-*m'*-, m.p. 171—172°, and -*p'*-nitro-, m.p. 165—166°, -*o*- m.p. 201—202°, -*m'*-, m.p. 176—177°, and -*p'*-amino-, m.p. 155—156° (*dihydrochloride*, decomp. from 200°), -*o*-, m.p. 182—183°, -*m'*-, m.p. 195—196°, and -*p'*-hydroxyanilide (VI), m.p. 196—197°. With hot Ac₂O (IV)

gives *p*-acetamidobenzenesulphon-*p'*-acetamidoanilide, m.p. $>260^\circ$. Diazotisation of (II), (III), and (IV) affords the *o*-diazomide, decomp. $138-140^\circ$, (V), and (VI), respectively. (IV) is moderately effective against streptococcal infections in mice. R. S. C.

Influence of metal sulphates and vanadium pentoxide on sulphonation of α -naphthylamine.—See B., 1938, 884.

Coupling of methone with tetrazonium compounds. B. H. IYER (J. Indian Inst. Sci., 1938, 21, A, 65–75).—"Methone" (3-hydroxy-5:5-dimethyl- Δ^2 -cyclohexenone) (I) couples with *p*-C₆H₄R·N₂Cl to yield the 2-*p*-nitro-, m.p. $215-216^\circ$, and 2-*p*-acetamido-benzeneazo- (II), m.p. $250-255^\circ$, -derivatives, respectively. (II) is hydrolysed (30% H₂SO₄) to the *p*-NH₂-compound (III), m.p. 225° , which when diazotised and coupled with (I) yields the corresponding *p*-phenylenebisazo-derivative, m.p. $275-280^\circ$ (decomp.). Similarly, (I) coupled with tetrazotised benzidine, *o*-tolidine, and *o*-dianisidine yields diphenylene- (IV), m.p. 285° (decomp.), 3:3'-dimethyldiphenylene- (C₆H₄Me₂), m.p. $263-265^\circ$ (decomp.), and 3:3'-dimethoxydiphenylene-4:4'-bisazo-, m.p. $290-292^\circ$ (decomp.), -derivatives of (I). Reduction of (IV) (SnCl₂-HCl) yields benzidine and 2-amino-5:5-dimethyldihydroresorcinol. The above dyes on silk and wool give yellow to orange shades fast to light and washing, but fugitive on cotton; (III) dyes leather light-fast yellow shades. With (I) (1 mol.) in EtOH; benzidine and *o*-tolidine yield respectively 3-(4'-amino)-, m.p. $217-218^\circ$, and 3-(4'-amino-3:3'-dimethyl)-*p*-diphenylamino-5:5-dimethyl- Δ^2 -cyclohexenone, m.p. 245° , whilst with 2 mols. of (I), NN'-di-(3-keto-5:5-dimethyl- Δ^2 -cyclohexenyl)-benzidine, m.p. $339-341^\circ$ (decomp.), and *o*-tolidine, m.p. 320° (decomp.), respectively, are formed.

J. D. R.

Hydrolysis of diazo-compounds, and their activity. A. A. TSCHERKASSKI (Prom. Org. Chim., 1938, 5, 322–325).—The readiness with which diazo-compounds undergo coupling parallels the degree of hydrolysis of the diazonium salt in aq. solution; this process consists of the steps $R\cdot NX:N \rightleftharpoons syn-R\cdot N\cdot NX \rightarrow syn-R\cdot N\cdot N\cdot OH$ (I). The relative concn. of (I) in aq. solutions, and hence the activity of a given diazo-compound, rises with increasing concn. of the latter, and with increasing negativity of R, for a series of compounds. R = *m*-C₆H₄Me and 3:5-C₆H₃Me₂ are exceptions to this rule. R. T.

Mechanism of the diazoaminobenzene conversion: addendum. H. V. KIDD (J. Org. Chem., 1938, 2, 577; cf. A., 1937, II, 494). R. S. C.

Preparation of 2:4-dinitro-6-cyclohexyl-phenol.—See B., 1938, 888.

Thermal decomposition of diphenyl ether. E. STAROKADOMSKAJA (J. Appl. Chem. Russ., 1938, 11, 646–651).—Decomp. of Ph₂O takes place only very slowly in glass vessels at $<440^\circ$. R. T.

Isolation of guaiacol and pyrogallol 1:3-dimethyl ether from hardwood waste sulphite pulp liquor.—See B., 1938, 894.

M** (A., II.)

Antisterility factor (vitamin-E). V. Synthetic antisterility factor. W. JOHN and P. GÜNTHER (Z. physiol. Chem., 1938, 254, 51–56).—2:3-Dimethyl-1:4-naphthaquinone was hydrogenated (colloidal Pt, AcOH) to 1:4-dihydroxy-2:3-dimethyl-5:6:7:8-tetrahydronaphthalene, m.p. $190-191^\circ$, absorption max. 288 m μ . (oxidised to the corresponding quinone, m.p. 121°), converted into the mono-, m.p. 78° , absorption max. 283 m μ ., and di-n-dodecyl ether, m.p. 57° , absorption max. 296 m μ . The mono-ether is active in promoting fertility in female rats on a vitamin-E-free diet in doses of 60–80 mg., i.e., it is 3–5% as active as α -tocopherol. The specificity of -E is discussed. F. O. H.

Synthetic substances with vitamin-E activity. F. VON WERDER and T. MOLL (Z. physiol. Chem., 1938, 254, 39–50).—The following were active in 100-mg. doses (increase in fertility of female rats on a vitamin-E-free diet): duroquinone; 2:3-dimethyl-quinol; 1:4-dihydroxy-2:3-dimethyl-5:6:7:8-tetrahydronaphthalene, m.p. 190° [obtained by reduction (H₂, PtO₂, AcOH) of 2:3-dimethyl-1:4-naphthaquinone]; mono-, m.p. $81-82^\circ$, and di-n-butyl, m.p. 58° , mono-, m.p. 82° , and di-n-hexyl, m.p. 47° , di-n-heptyl, m.p. 56° , mono-, m.p. 88° , and di-n-octyl, m.p. 64° , n-dodecyl (acetate, m.p. $95-96^\circ$; allophanate, m.p. 223°), dihydrophytyl, benzyl (acetate, m.p. 118°) and dihydrochaulmoogryl, m.p. 89° (acetate, m.p. $60-61^\circ$), ethers of duroquinol; n-hexyl, m.p. 73° , and n-dodecyl, m.p. $81-82^\circ$ (and its acetate, m.p. 47° , and propionate, m.p. 47°), ethers of ψ -cumoquinol. ψ -Cumoquinol dihydrochaulmoogryl ether, m.p. 61° , and duroquinol n-dodecyl ether palmitate, m.p. 86° , are active in 50-mg. doses whilst the n-heptyl, m.p. $82-83^\circ$, dibenzyl, and di-n-dodecyl ethers, and the n-dodecyl ether propionate, m.p. $80-80.5^\circ$, of duroquinol, and ψ -cumoquinol di-n-dodecyl ether, m.p. 47° , are inactive. No relationship between activity and structure of the above compounds is apparent.

F. O. H.

Hydroxyalkyl ethers of basic phenols. Antipneumococcal activity of some 8-quinolyl ethers. C. L. BUTLER and (Miss) A. G. RENFREW (J. Amer. Chem. Soc., 1938, 60, 1582–1585).—*p*-C₆H₄Me·SO₃·[CH₂]₂·O·CH₂Ph (I) and KOH-EtOH convert PhOH and NHAc·C₆H₄·OH in good yield into Ph, b.p. $175^\circ/3$ mm., and *p*-acetamidophenyl β -benzyloxyethyl ether, m.p. 88° , respectively, the latter product with 11% HCl giving 80% of *p*-NH₂·C₆H₄·O·[CH₂]₂·OH, m.p. 73° (Ac₂ derivative, m.p. 128°). Similar alkylation and hydrolysis give good yields of 8-quinolyl β -hydroxyethyl (II), m.p. $83-84^\circ$ (hydrochloride, m.p. $199-200^\circ$; Ac derivative, m.p. 153°), β -hydroxyisopropyl, m.p. 65° (hydrochloride; Ac derivative, m.p. 99°), and γ -hydroxy-n-propyl ether, m.p. 129° (hydrochloride; Ac derivative, an oil). *p*-C₆H₄Me·SO₃Et gives 8-ethoxyquinoline. *p*-NH₂·C₆H₄·OH and (I) give a poor yield of *p*- β -benzyloxyethoxy-NN-di- β -benzyloxyethylaniline (H sulphate), hydrolysed to *N*-*p*- β -hydroxyethoxyphenylmorpholine (*p*-toluenesulphonate, amorphous; acetate, m.p. $118-119^\circ$). *m*-NEt₂·C₆H₄·OH gives 62% of *m*-diethylaminophenyl β -hydroxyethyl ether, m.p. 41° , b.p. $148^\circ/3$ mm. (oily Ac derivative), by means of (I) or CH₂Cl·CH₂·OH

(III). (III) gives, however, only 19% of (II) and only 12.5% of $\text{OPh}(\text{CH}_2)_2\text{OH}$ (cf. Rindfusz, A., 1919, i, 342). Failure of (III) to alkylate phenolic cinchona alkaloids smoothly is thus due to interference by the N. Alkylation reduces the pneumococcicidal activity and toxicity (mice) of 8-hydroxyquinoline, but the Et and $\text{OH}\cdot\text{C}_2\text{H}_4$ ethers retain some activity. R. S. C.

Mobility of groups containing sulphur. V. D. T. GIBSON (J.C.S., 1938, 983—986; cf. A., 1938, II, 135).—The rate of reaction of $\text{COPh}\cdot\text{CH}_2\text{Ph}$ (I) with $\text{CH}_2(\text{SO}_2\text{Et})_2$, $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{COMe}$ (II) in presence of RCO_2Na is the greater the more alkaline is the solution, i.e., $\text{R} = \text{Et} > \text{Me} > \text{H}$. Similarly, (I) and $(\text{OMe}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{SO})_2$ in presence of NaOAc give the mono-, whereas stronger alkali leads to the disubstitution product. The Brooker-Smiles reaction (A., 1926, 947) for various compounds is faster in $\text{C}_5\text{H}_5\text{N}$ than in EtOH , indicating that conjugation of the lone pair of electrons on the entering S with the double linking of the enolised substitution product is a favouring, but not essential, factor in the reaction. The rates of reaction of Me and 2:5- $\text{C}_6\text{H}_3\text{Cl}_2$ camphor-thiolsulphonates with $\text{CH}_2(\text{COPh})_2$, $\text{CH}_2(\text{CO}_2\text{Et})_2$, $\text{CH}_2(\text{SO}_2\text{Et})_2$, and (II) in 85% $\text{COMe}_2 + \text{NaOAc}$ (no reaction with HCO_2Na except in 80% $\text{C}_5\text{H}_5\text{N}$) show that $\text{S}\cdot\text{C}_6\text{H}_3\text{Cl}_2$ enters more rapidly than SMe even when the possibility of conjugation is absent; the difference is least marked with (II) (development of conjugation with substitution). Previous results (*loc. cit.*) are supplemented.

$p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{NO}_2$ is conveniently prepared from $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Na}$ and $\text{CH}_2\text{Br}\cdot\text{NO}_2$ in warm EtOH . R. S. C.

Reaction of α -naphthylamine-5-sulphonic acid with sodium hydrogen sulphite. I. M. KOGAN and A. I. NIKOLAIEVA (J. Appl. Chem. Russ., 1938, 11, 652—659).—1:5- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{Na}$ is obtained in 85% yield from 1:5- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{Na}$ (1 mol.) and NaHSO_3 (20 mols.), at 100° and p_{H} 4.2. Smaller amounts of NaHSO_3 may be used provided this p_{H} is attained by addition of AcOH , NaHSO_4 , or $\text{Al}_2(\text{SO}_4)_3$. R. T.

Bromination of optically active phenylmethyl- and phenylpropyl-carbinols. P. A. LEVENE and A. ROTHEN (Science, 1938, 87, 510).— $\text{CHPhPr}\cdot\text{OH}$ (I) and higher homologues react predominantly with HBr (gas) without inversion. At 0° the reaction with (I) is practically instantaneous and the rotation of the CHPhPrBr (II) formed increases markedly with fall in temp. to -65° , with (I) and (II) rotating in the same direction. At temp. $> -35^\circ$, the rotation of CHPhMeBr , formed from $\text{CHPhMe}\cdot\text{OH}$ under similar conditions, is opposite to that of the carbinol; the bromide shows a small increase in rotation at lower temp. At $> -35^\circ$ the rotation of the bromide changes sign, the reaction then proceeding without inversion. At each temp. two simultaneous reactions take place, one with and one without inversion; at lower temp., the latter predominates. L. S. T.

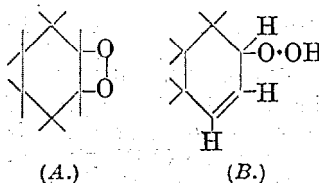
$\gamma\gamma\gamma$ -Triphenylpropyl derivatives. C. B. WOOSTER, H. D. SEGOL, and T. T. ALLAN, jun. (J. Amer. Chem. Soc., 1938, 60, 1666—1667).—The structure of $\gamma\gamma\gamma$ -triphenyl-*n*-propyl alcohol (I) (A.,

1934, 1095) is confirmed. It is obtained (m.p. $106.5\text{--}107.5^\circ$) from CPh_3Na and $(\text{CH}_2)_2\text{O}$ in liquid NH_3 , is converted by HI into the known iodide, and by boiling Ac_2O into the acetate, m.p. $114\text{--}115^\circ$ (also obtained from the iodide by AgOAc), whence it is regenerated by NaOH -aq. EtOH . BzCl gives (?) the benzoate, m.p. 134° . (I) is stable at $150\text{--}170^\circ$ and gives no CHPh_3 with KNH_2 in liquid NH_3 . R. S. C.

Magnesium derivative of bromopentamethylbenzene. H. CLEMENT (Bull. Soc. chim., 1938, [v], 5, 1011—1020).—A reprint of the paper by Savard and Hösögüt (A., 1938, II, 275). H. W.

Fission of alicyclic ethers. W. HÜCKEL and H. BRETSCHNEIDER (J. pr. Chem., 1938, [ii], 151, 61—64).— PhOMe is hydrogenated (Ni, $170\text{--}180^\circ/70$ atm.) to hexahydroanisole (I); this gives a compound, m.p. -14° , with BF_3 which decomposes when warmed into a methoxydimethyldodecahydrotriphenylene, m.p. 159° . BzCl , (I), and ZnCl_2 in CHCl_3 yield MeCl , cyclohexyl chloride and benzoate, and MeOBz . *l*-Menthhol (II) is transformed by the successive action of NaNH_2 in PhMe and EtBr into *l*-menthyl Et ether (III), b.p. $87.5^\circ/11$ mm., $[\alpha]_D^{25} -100^\circ$. Addition of HgEt_2 or PbEt_4 in cyclohexane (IV) to (III) + Na in (IV) yields (II) and 3-ethylmenthane (V). *d*-Neomenthyl Et ether, b.p. $84.5^\circ/11$ m.m., $[\alpha]_D^{25} +30.5^\circ$, similarly yields neomenthol and (V). Oxidation of (III) with CrO_2Cl_2 in CCl_4 gives *l*-menthone. H. W.

Autoxidation of hydrocarbons. cycloHexene peroxide, particularly its decomposition by alkalis. II. H. HOCK and K. GÄNICKE (Ber., 1938, 71, [B], 1430—1437).—cycloHexene peroxide (5 mols.) is disproportionated by aq. 1.5% NaOH to Δ^2 -cyclohexenol (I) (3 mols.) and acids (2 mols.) including CO_2 , HCO_2H , AcOH , glutaric, adipic (II), and α -hydroxyadipic (III) acid, (II) and (III) appearing to be derived from the peroxide forms (A) and (B), respectively. The production of *trans*-cyclohexane-1:2-diol, m.p. $103\text{--}104^\circ$, is established. Na_2CO_3 also causes the production of (I) but less



acid is produced, the intermediate CO-compounds being resinified to a greater extent owing to the slower oxidation. The slow auto-decomp. of the peroxide in absence of acid or alkali probably proceeds similarly; the isolation of $p\text{-O}\cdot\text{C}_6\text{H}_4\cdot\text{O}$ is of interest. H. W.

Synthesis of compounds related to the anti-rachitic vitamins. $\alpha\beta$ -Di- Δ^1 -cyclohexenylethylene. G. N. BURKHARDT and N. C. HINDLEY (J.C.S., 1938, 987—991).—1-Acetylenylcyclohexanol (I), cyclohexanone, and KO^tBu^* in boiling Et_2O give 70% of $\alpha\beta$ -di-1-hydroxycyclohexylethylene, m.p. 109° , the diacetate, m.p. 47° , b.p. $130\text{--}135^\circ/0.5$ mm., of which is unchanged by Cu at $<180^\circ$, but with 1 mol. of H_2 in presence of $\text{Pd}\text{--}\text{CaCO}_3$ in MeOH gives $\alpha\beta$ -di-1-acetoxycyclohexylethylene (II), b.p. $143\text{--}145^\circ/1$ mm. [hydrolysed to the $(\text{OH})_2$ -compound (III), m.p. 153°]. With Cu-bronze at $145\text{--}150^\circ/30$ mm. (II) gives AcOH and 80% of $\alpha\beta$ -di- Δ^1 -cyclohexenylethylene, b.p. $110\text{--}115^\circ/1$ mm., m.p. 29° , unstable [absorption max. at

2595, 2690 (ϵ 42,600), and 2810 A.], converted at 255° in N₂ into an oily substance [absorption max. at 2600—2700 (ϵ 12,600) and 2800 A.], which with Se at 290—320° gives phenanthrene. With boiling, aq. H₂C₂O₄, KHSO₄ at 140°, I at 160°, or PBr₃ in C₅H₅N, (III) gives $\alpha\beta$ -dicyclohexylethylene 1:1'-oxide, b.p. 116—118°/10 mm. (dibromide, m.p. 96°), which absorbs 2 H₂ catalytically, probably with fission of the oxide ring. With SOCl₂ in Et₂O-C₅H₅N, (III) gives the ester, $[\text{CH}_2]_5 > \text{C} \begin{smallmatrix} \text{O-SO}_2\text{O} \\ \text{CH-CH} \end{smallmatrix} < \text{C} < [\text{CH}_2]_5$, m.p. 83°, readily hydrolysed to (III). 2-Methylcyclohexanone (IV) gives, by Cook and Lawrence's method (A., 1938, II, 107); 2-methyl-1-acetylenylcyclohexanol (V), b.p. 69—71°/10 mm., m.p. 57°, and stereoisomeric forms [one form (VI), m.p. 149°, obtained pure] of $\alpha\beta$ -di-1-hydroxy-2-methylcyclohexylacetylene, obtained also from (IV), (V), and NaNH₂. (IV) and (V) or (I) and (IV) with KOBu⁺ give a crude product, containing (VI), indicating that the C₂H₂-ketone condensation is reversible. (IV) and (I) with NaNH₂ in Et₂O give a mixture of forms of α -1-hydroxycyclohexyl- β -1-hydroxy-2-methylcyclohexylacetylene, b.p. 186—189°/15 mm., whence one form, m.p. 97.5°, was obtained pure; (V) and cyclohexanone give a poor yield of a similar mixture, also obtained from the Grignard derivative of (I). R. S. C.

Catalytic reduction of aryl alkyl ketones in presence of amines. Synthesis of ephedrine. P. COUTURIER (Compt. rend., 1938, 207, 345—347).—COPhMe with Raney Ni in conc. NH₃-MeOH affords CHPhMe·NH₂ (15%) and CHPhMe·OH (40%); *o*- and *p*-OMe·C₆H₄·COMe react similarly but with difficulty. CH₂Ph·COMe (I) affords CH₂Ph·CHMe·NH₂ nearly quantitatively. *o*-OH·C₆H₄·COEt (II) reacts like (I), but *m*-OH·C₆H₄·COEt affords only *m*-OH·C₆H₄·CHEt·OH, whilst the *p*-isomeride reacts very slowly; α -*o*- and *p*-hydroxyphenylpropylamine [Bz₂ derivatives, m.p. 124—129° and 178—179° (decomp.), respectively] decompose when heated, or in cold HCl, to NH₃ and propenylphenols. (II) with a small excess of NH₂Et affords α -*o*-hydroxyphenylpropylethylamine, undistillable (Ac derivative, m.p. 108°). The reduction of COPh·COMe in presence of EtOH-Raney Ni containing NH₂Me affords dl-ephedrine because the CO adjacent to Ph reacts as in COPhMe whereas that adjacent to Me reacts as in (I) (cf. Skita *et al.*, A., 1933, 716). J. L. D.

Structure of nitrones. G. VON FODOR and P. CSOKÁN (Annalen, 1938, 535, 284—290).—Absorption spectra indicate that products from RCHO and OH·CHAR·CHMe·NH·OH are $\text{O} \begin{smallmatrix} \text{CHAR} \cdot \text{CHMe} \\ \text{CHR} \cdot \text{N} \cdot \text{OH} \end{smallmatrix}$, whereas those from OAc·CHAR·CHMe·NH·OH have the nitron structure, OAc·CHAR·CHMe·NO·CHR. *o*-OH-aldehydes give products, OH·CHAR·CHMe·NO $\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} > \text{C}_6\text{H}_4 \cdot \text{o}$. R. S. C.

Phenanthrene series. XVII. Amino-alcohols derived from 9-hydroxy-1:2:3:4-tetrahydrophenanthrene. A. BURGER (J. Amer. Chem. Soc., 1938, 60, 1533—1536; cf. A., 1938, II, 321).—The Me ester, m.p. 42—43°, of β -4-methoxy-1-naphthoyl-

propionic acid in presence of 16% Pd-C in EtOH absorbs >2 H₂, giving esters of oily acids; it is not reduced by H₂-Cu-Cr₂O₃ at 100°, and at 156—210° gives (?) impure methoxytetrahydronaphthylbutyrolactone, m.p. 120—122°. The acid is reduced (modified Clemmensen) to γ -4-methoxy-1-naphthylbutyric acid in 50% yield. 1-Keto-9-acetoxy-1:2:3:4-tetrahydrophenanthrene (I), m.p. 159—160°, is obtained from the OH-compound, Ac₂O, and C₅H₅N. 1-Keto-9-methoxy-1:2:3:4-tetrahydrophenanthrene (II) and Br in Et₂O give the 2-Br-derivative, m.p. 174—175°, converted by NHEt₂ in boiling C₆H₆ into 2-diethylamino-1-keto-9-methoxy-1:2:3:4-tetrahydrophenanthrene (30% yield), m.p. (crude) 90—95° [hydrochloride, m.p. 128—138° (decomp.)], and 1-hydroxy-9-methoxyphenanthrene, m.p. 131—132° [Ac derivative, m.p. 154.5—155.5°, converted by 48% HBr-AcOH into 1:9-dihydroxyphenanthrene, m.p. 184—185° (evacuated tube; sinters at 181°) (Ac₂ derivative, m.p. 154—155°; Me₂ ether, m.p. 113—114°)]. 2-Bromo-9-hydroxy-1-keto- (prep. by Br in CHCl₃-Et₂O), m.p. >330° (after decomp.), and 2-piperidino-1-keto-9-methoxy-1:2:3:4-tetrahydrophenanthrene (60% yield), m.p. 112—113° [hydrochloride, m.p. 258—261° (decomp.; sinters at 246°)], unstable in O₂, are similarly prepared. Hydrogenation of the NH₂-ketones could not be arrested at the alcohol stage. With paraformaldehyde and the appropriate sec. amine in iso-C₅H₁₁·OH (I) and (II) yield 20—70% of 1-keto-9-methoxy-2-1':2':3':4'-tetrahydroisoquinolino- [hydrochloride, m.p. 176—177° (decomp.); perchlorate, m.p. 135—150° (decomp.)], and -2-diethylamino-methyl-1:2:3:4-tetrahydrophenanthrene, m.p. 83° (hydrochloride, m.p. 160—161°), 1-keto-9-acetoxy-2-1':2':3':4'-tetrahydroisoquinolino-, m.p. 144° [hydrochloride, m.p. 167—168° (decomp.)], and 2-diethylamino-methyl-1:2:3:4-tetrahydrophenanthrene (hydrochloride, m.p. 146—147°), hydrogenated (PtO₂) in MeOH to 1-hydroxy-9-methoxy-, m.p. 137—138° [hydrochloride, m.p. 211°; Ac derivative hydrochloride, m.p. 200—201° (decomp.)], -9-acetoxy- [hydrochloride, m.p. 234—235° (decomp.)], and -9-hydroxy-2-1':2':3':4'-tetrahydroisoquinolinomethyl-1:2:3:4-tetrahydrophenanthrene, m.p. 213° (decomp.; in vac.) [hydrochloride, m.p. 225—227° (decomp.)], and 1-hydroxy-9-methoxy-2-diethylaminomethyl-1:2:3:4-tetrahydrophenanthrene [hydrochloride, m.p. 190° (decomp.); Ac derivative hydrochloride, m.p. 165—166° (decomp.)]. The oxime, m.p. 174—175°, of (II) with Al-Hg in moist Et₂O gives 1-amino-9-methoxy-1:2:3:4-tetrahydrophenanthrene [hydrochloride, m.p. 291° (decomp.; in vac.)]. R. S. C.

Reactions in sunlight. I. [Acetophenone and aromatic hydrocarbons.] E. OLIVERI-MANDALÀ. II. [Aromatic hydrocarbons.] E. OLIVERI-MANDALÀ, G. CARONNA, and E. DELEO (Gazzetta, 1938, 68, 324—327, 327—331).—I. Acenaphthene and COPhMe (I) in sunlight (August, Palermo) give a product, C₂₀H₁₈O [phenylacenaphthylmethylcarbinol (?)], m.p. 98—99°, and acenaphthylene. CH₂Ph₂ and (I) give a product, C₃₄H₃₀O [phenyl- $\alpha\alpha\beta\beta$ -tetraphenylethylmethylcarbinol (?)], m.p. 222—223°, and the pinacol of (I).

II. CH₂Ph₂ in C₆H₆ in sunlight (3 months) gives

(CHPh₂)₂. Fluorene similarly gives bisdiphenyleneethane. Acenaphthene is unchanged, but in presence of Bz₂ yields a *product*, C₂₆H₂₀O₂, m.p. 234°.

E. W. W.

Micro-determination of cholesterol by a new colour reaction. S. OHYAMA (J. Biochem. Japan, 1938, 27, 395—404).—The substance (in CHCl₃) is treated with salicylaldehyde (in CHCl₃), H₂SO₄, and H₂O, the mixture well shaken for 2 hr., and the CHCl₃ layer compared with suitable standards. The reddish-violet colour produced is stable and the error for samples containing 0.3—1.2 mg. of cholesterol is <5%. The colours with other aldehydes etc. are studied.

F. O. H.

Purification of crude sitosterol. P. LOBERT (Bull. Soc. Chim. biol., 1938, 20, 766—806).—Pure sitosterol (I) cannot be obtained from the unsaponifiable matter of oil of maize or barley rootlets by crystallisation. M.p. and [α]_D alone cannot be used as criteria of purity; spectrographic examination must also be made. When adsorption on Al₂O₃ + animal C (the column being examined in Wood's light) followed by acetylation and recrystallisation from EtOH is applied pure (I), m.p. 140.8—141°, [α]_D —38.8° in CHCl₃ (acetate, m.p. 140.2—140.4°, [α]_D —43.42° in CHCl₃), is obtained. In addition to (I), maize oil contains ergosterol (II) and a sterol having absorption max. at 2530, 2417, and 2354 Å. and barley oil also contains (II), a sterol with absorption bands at 2530, 2417, and 2352 Å., another with bands at 2707 Å., and another with bands at 3365, 3245, and 3109 Å.

W. McC.

Sterols. XXXV. Carbinols from stallions' urine. R. E. MARKER, E. J. LAWSON, E. ROHRMANN, and E. L. WITTLE. XXXVII. Uranediol from mares' pregnancy urine. R. E. MARKER, E. ROHRMANN, and E. L. WITTLE. XXXVIII. Pregnenediol in mares' pregnancy urine. Its conversion into progesterone. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1938, 60, 1555—1558, 1561—1564, 1655—1567; cf. A., 1938, II, 322).—XXXV. The neutral fraction from stallions' urine yields, besides a very little ketone (by Girard's reagent), carbinols from which digitonin ppts. β-*equistanol* (I), C₃₀H₅₄O, m.p. 133° (acetate, m.p. 124°; stable to Br; largely unaffected by Na in xylene), oxidised by CrO₃ in 90% AcOH to β-*equistanone*, C₃₀H₅₂O, m.p. 115°. (I) belongs to the *allo*-series, is probably a phytosterol or phytosterol derivative derived from the food, and may be identical with dihydro-α-tritisterol (Karrer *et al.*, *ibid.*, 13). The mother-liquors from which (I) is pptd. probably contain α-*equistanol*, since treatment with Na-xylene leads to more (I); they then yield also an *allo-triol*, C₂₁H₃₆O₃, m.p. 295° (triacetate, m.p. 140—145°), and an *allo-tetraol* (II), C₂₁H₃₆O₄, m.p. 290—295°, both giving insol. digitonides and thus being 3(β)-*allo*-compounds; their 3(α)-epimerides must have occurred in the urine. (II) may be *allopregnane*-3(β):11:20:21-tetraol derived from corticosterone. The epimerised carbinol mixture, not pptd. by digitonin, gives, when oxidised, uranetrione, m.p. 247°. Stallions' urine thus probably contains the same uranetriol as does mares' pregnancy urine, and this

triol is probably derived from the adrenal cortex or hormone of unknown function. β-Sitosterol and cholesterol are absent from stallions' urine.

XXXVII. The carbinol fraction of mares' pregnancy urine, freed from ketones, yields by digitonin *urane*-3(β):11-*diol* (III) (5 mg. per gal.), m.p. 210° (diacetate, m.p. 160°), largely unchanged by Na-xylene and thus normal at C₆₅, oxidised to uranedione, m.p. 177.5° [only *mono-semicarbazone*, m.p. 245° (decomp.), and -2:4-*dinitrophenylhydrazone*, m.p. 200° (decomp.)]. Hydrogenation (PtO₂) of the dione in AcOH affects only C₆₃, since Na-xylene destroys the product. Uranetriol and (III) are probably related to constituents of the adrenal cortex or to an unknown hormone. Examination of the mother-liquors from (III) indicates absence of other substances having a β-OH at C₆₃, and the coprostane structure at C₆₅.

XXXVIII. The carbinol fraction from mares' pregnancy urine also yields (after epimerisation) *allo*-pregnane-3(β):20(α)-*diol* (IV), m.p. 216° (oxidised to *allopregnenedione*), *pregnene*-3(β):20(α)-*diol* (V), m.p. 172—176°, (I), and, possibly, uranediol. (V) absorbs Br to give a substance converted by CrO₃-AcOH followed by Zn dust into progesterone, obtained directly by heating with Cu at 230°/20 mm. and then subliming at 125°/high vac. With H₂-PtO₂ at 3 atm. in EtOH (V) yields (IV). Cholesterol is absent from mare's pregnancy urine.

R. S. C.

Dialkylaminoalkyl esters of phenyl-substituted fatty acids.—See B., 1938, 981.

Salts of nitro-compounds. III. Reaction of the silver salt of phenylnitroacetonitrile with diphenylbromomethane. R. L. SHRINER and G. B. BROWN (J. Org. Chem., 1938, 2, 560—568; cf. A., 1938, II, 88).—CN·CPh·NO·OAg and CHPh₂Br in C₆H₆ at <20° give up to 18% of the *C*-alkylation product, α-nitro-αββ-triphenylpropionitrile (I) (cf. Wieland *et al.*, A., 1933, 1163), and 50% of the *O*-alkylation product, CN·CPh·NO·O·CHPh₂, which is not isolated as such but is indicated by its decomp. products, CPh₂ and CN·CPh·N·OH; CHPh₂·OH and (CHPh₂)₂O (produced by hydrolysis of CHPh₂Br) and a (?) polymeride, m.p. 245—249° (after decomp.), of CPh·CN were also isolated. The structure of (I) follows from (a) its conversion by KOH-EtOH into KNO₂ and triphenylacrylonitrile (II), m.p. 165—166°, which is obtained also by HI-red P in AcOH and from CPh₂, CH₂Ph·CN, and NaNH₂, and (b) its hydrogenation (PtO₂) in AcOH to αββ-triphenylpropionitrile (III), m.p. 101.5—102° (obtained alone in EtOH), and acet-βγγ-triphenylpropylamide (IV), m.p. 143.5—144°. Conc. HCl at 170° hydrolyses (III) to the amide, also prepared from the acid (prep. from CHPhPr·CHBr·CO₂H, C₆H₆, and AlCl₃ at 60°). H₂-Raney Ni reduction of (III) at 120°/2500 lb. and acetylation give (IV). Pyrolysis of (I) at 160° gives NO₂, (II), C₂Ph₄, CPh₂, and BzOH; there is no evidence of dissociation of (I) into radicals; HI gives no CH₂Ph₂ and it is unaffected by O₂ in hot C₆H₆.

R. S. C.

Isomeric triazocinnamic acids and related compounds. K. A. N. RAO and P. R. VENKATARAMAN (J. Indian Chem. Soc., 1938, 15, 194—204).—Triazo-cinnamic and -benzoic acids are synthesised

from the diazotised NH_2 -acids and NaN_3 . *o*-Triazocinnamic acid (I), m.p. 186° (decomp.) [dibromide, m.p. 165 – 166° (decomp.)], is reduced by $(\text{NH}_4)_2\text{S}$ to the NH_2 -acid, by $\text{Sn} + \text{HCl}$ to carbostyryl, and by Na-Hg to dihydrocarbostyryl; *m*- (II), m.p. 165° (decomp.) (dibromide, m.p. 157°), and *p*-triazocinnamic acid (III), decomp. 195 – 196° (slight decomp. 160°) (dibromide, m.p. 140 – 141°), with $\text{Sn} + \text{HCl}$ yield $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, and with Na-Hg , $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$. All three are oxidised (cold KMnO_4) to the $\text{N}_3\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. An acid, decomp. 268 – 270° , is a by-product in the prep. of (II). (III) and *o*-, m.p. 143 – 144° , *m*-, m.p. 160° , and *p*-, m.p. 180 – 181° , triazobenzoic acids with conc. H_2SO_4 evolve $\frac{2}{3}$ of their N, whilst (I) and (II) evolve about $\frac{1}{2}$. The *p*-acid is the least stable of the cinnamic series, but the most stable of the benzoic series. $\text{Ph}[\text{CHBr}]_2\cdot\text{CO}_2\text{H}$ with NaN_3 in $\text{EtOH-C}_5\text{H}_5\text{N}$ yields an acidic compound (containing N but not the N_3 group), m.p. 217° (dibromide, m.p. 176°), and a little $\text{CHPh}\cdot\text{CHBr}$. $\text{Ph}[\text{CHBr}]_2\cdot\text{CO}_2\text{Me}$ with NaN_3 in MeOH , followed by $\text{C}_5\text{H}_5\text{N}$, yields *Me* α - or β -triazocinnamate (oil). A. Lr.

Condensation of aldehydes with malonic acid in presence of organic bases. X. Condensation of resorcyaldehyde. K. C. PANDYA and T. S. SODHI (Proc. Indian Acad. Sci., 1938, 7, A, 381–383; cf. A., 1935, 353; 1937, II, 340).—Resorcyaldehyde (I) (1 mol.) with $\text{CH}_2(\text{CO}_2\text{H})_2$ (1 mol.) and $\text{C}_5\text{H}_5\text{N}$ (0.15 mol.) at 100° affords umbelliferone (II) (43%). The yield is diminished without $\text{C}_5\text{H}_5\text{N}$ or in presence of piperidine. (I) with NaOAc and Ac_2O at 160 – 180° affords 7-acetoxycoumarin, hydrolysed (10% KOH) to umbellic acid (III). (I), $\text{CH}_2(\text{CO}_2\text{H})_2$, and AcOH at 100° afford (III) (54%). Robinson and Shinoda's method (A., 1925, i, 1301) of condensation gave no isolable product. J. L. D.

Condensation of aldehydes with amides. I. Salicylaldehyde. K. C. PANDYA and T. S. SODHI. II. Cinnamaldehyde. R. K. MEHRA and K. C. PANDYA (Proc. Indian Acad. Sci., 1938, 7, A, 361–368, 376–380).—I. *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (I) with NH_2Bz alone or with a trace of lutidine at 130 – 140° affords only the α -form of salicylidenebenzamide, whereas in the presence of anhyd. NaOAc , $\text{C}_5\text{H}_5\text{N}$, or piperidine, a mixture of the α - and β -forms results (cf. J.C.S., 1908, 93, 1933). $\text{R}\cdot\text{CO}\cdot\text{NH}_2$ ($\text{R} = \text{H}$, Me , Et , CH_2Ph) and (I) similarly afford salicylidene-formamide, -acetamide, decomp. 160 – 170° (lit. 150°), -propionamide, decomp. 190 – 195° , and -phenylacetamide, m.p. 110 – 114° , respectively. The presence of the org. base gives a better yield of a purer product at a lower temp.

II (cf. J.C.S., 1921, 119, 298). $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ (I) (1 mol.) with $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}_2$ (2 mols.) at 130 – 140° affords cinnamylidenebisphenylacetamide in 18.7% yield, which is not improved by catalytic org. bases. (I) (1 mol.) with NH_2Ac (4 mols.) and $\text{C}_5\text{H}_5\text{N}$ (0.15 mol.) at 120 – 125° affords cinnamylidenebisacetamide (52%), m.p. 234° . (I) (1 mol.) with NH_2Bz (2 mols.) at 110 – 140° affords cinnamylidenebisbenzamide (50.5%), m.p. 250° ; $\text{C}_5\text{H}_5\text{N}$ (0.15 mol.) improves the yield to 55%. Similarly, (I) and $\text{EtCO}\cdot\text{NH}_2$ at 100° afford cinnamylidenebispropionamide (46%), m.p.

220 – 221° , and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHO}$ with NH_2Bz at 140 – 150° (no $\text{C}_5\text{H}_5\text{N}$) affords γ -phenylpropylidenebisbenzamide (39%), m.p. 244 – 245° . J. L. D.

Derivatives of β -amino- α -hydroxy- α -phenylpropionic acid. II. B. CIOCCA and E. BROGGI (Annali Chim. Appl., 1938, 28, 230–238).—The following esters of β -dimethylamino- α -hydroxy- α -phenylpropionic acid were prepared (cf. A., 1936, 1377); *Et*, b.p. $120^\circ/1$ mm., *Bu*, b.p. 138 – $140^\circ/0.8$ mm., *Bu*^B, b.p. $140^\circ/1.5$ mm., and isoamyl, b.p. $140^\circ/0.8$ mm. The pharmacological properties of the corresponding *Ac* derivative hydrochlorides, m.p. 128° , 138° , 155° , and 135 – 136° , respectively, were studied in rabbits. The depressor action increases with increase in length of the mol. of esterifying alcohol with straight-chain alcohols but is considerably diminished with branched-chain alcohols.

F. O. H.

Synthetic and hydrolytic experiments with chymotrypsin. M. BERGMANN and J. S. FRUTON (J. Biol. Chem., 1938, 124, 321–329).—Cryst. chymotrypsin effects the synthesis of benzoyl-*l*-tyrosylglycineanilide, m.p. 226° , from benzoyl-*l*-tyrosine and glycineanilide at 37° and p_H 7.6, whilst under the same conditions no synthesis of benzoyl-*l*-tyrosineanilide from benzoyltyrosine and NH_2Ph occurs. Chymotrypsin does not hydrolyse benzoyl-*l*-tyrosineamide, m.p. 198° , $[\alpha]_D^{25} -24.6^\circ$, or benzoyl-*d*-, m.p. 215° , $[\alpha]_D^{25} +10.4^\circ$, or -*dl*-tyrosylglycineamide, whilst benzoyl-*l*-tyrosylglycineamide, m.p. 216° , $[\alpha]_D^{25} -10.2^\circ$, is split; the *dl*-compound is probably a very stable racemate. Benzoyl-*dl*-tyrosylglycineamide is stable to papain-HCN whilst the *l*-isomeride is completely hydrolysed at one peptide linking, and a similar effect, although not so marked, is observed with *l*- and *dl*-benzoylalanineamide. Benzoyl-*d*-tyrosylglycineamide is not attacked by papain and the *d*-tyrosyl residue has the same inhibitory influence as the *d*-amino-acid residue on the hydrolysis of carbobenzyloxy-*d*-leucylglycylglycine and on the enzymic anilide formation from benzoyl-*d*-phenylalanyl-glycine and from acetyl-*d*-phenylalanyl-*l*-glutamic acid. The following compounds were prepared and, in some cases, examined for chymotryptic and papain-hydrolysis. Benzoyl-dehydrotyrosineamide, m.p. 230° , *dl*-, m.p. 238° , and -*d*-tyrosineamide, m.p. 198 – 200° , $[\alpha]_D^{25} +24.4^\circ$, -*d*-tyrosine *Me* ester, m.p. 150 – 151° , -*dl*-tyrosylglycine *Et* ester, m.p. 157 – 158° , -*d*-, m.p. $\sim 250^\circ$, and -*l*-tyrosine hydrazide, m.p. $\sim 255^\circ$, -*d*-, m.p. 184° , and -*l*-tyrosylglycine *Et* ester, m.p. 184 – 185° , -dehydro-phenyl-alanineamide, m.p. 164° , and -alanylglycine *Et* ester, m.p. 140° , -*dl*-phenylalanyl-glycine-amide, m.p. 179° , and *Et* ester, m.p. 162° . All $[\alpha]$ are in MeOH .

T. F. D.

Enzymic synthesis of peptide linkings. M. BERGMANN and H. FRAENKEL-CONRAT [with D. G. DOHERTY] (J. Biol. Chem., 1938, 124, 1–6).—In presence of papain-cysteine (cf. A., 1938, III, 393), a peptide linking is formed between benzoyl-*l*-leucine and *l*-leucineanilide acetate, m.p. 121° (obtained by hydrogenating carbobenzyloxy-*l*-leucineanilide in MeOH-AcOH), which give benzoyl-*l*-leucyl-*l*-leucineanilide, m.p. 203° , $[\alpha]_D^{25} -44.5^\circ$ in AcOH , also obtained from benzoyl-*l*-leucine azide (A., 1936, 596) and

l-leucineanilide (from its acetate, above). With papain-cysteine, *glycineanilide acetate*, m.p. 136—137° (from carbobenzyloxyglycineanilide, hydrogenated in MeOH-AcOH), and benzoyl-*l*-leucine give, by a new type of enzymic reaction, in which the last replaces the glycine residue, *benzoyl-l-leucineanilide*, m.p. 212.5°. Further peptide syntheses by papain-cysteine are the conversion, in presence of NH_2Ph , of acetyldehydrophenylalanylglutamic acid into its *anilide* (I), m.p. 204°, $[\alpha]_D^{25} -108.2^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and of acetyl-*l*-phenylalanyl-*l*-glutamic acid into its *anilide* (II), m.p. 230°, $[\alpha]_D^{25} -25.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Hydrogenation (Pd-MeOH-AcOH) of (I) gives a mixture of stereoisomeric *acetylphenylalanyl-l-glutamic acid anilides*, m.p. 231°, $[\alpha]_D^{25} -113.9^\circ$ (+0.5 H_2O), and -27.1° (anhyd.), both in $\text{C}_5\text{H}_5\text{N}$; the rotation of the last suggests its identity with (II). *p*-Toluenesulphonyl-glycine with NH_2Ph in presence of papain-cysteine and a citrate buffer slowly gives its *anilide*, m.p. 156—157°; thus enzymic synthesis is apparently possible when the CO-NH group of the substrate is replaced by SO_2NH . E. W. W.

Asymmetric course of the enzymic synthesis of peptide linkings. M. BERGMANN and O. K. BEHRENS [with D. G. DOHERTY] (J. Biol. Chem., 1938, 124, 7—10).—Acetamidocinnamic acid azlactone and glycine in COMe_2 and 0.5N-NaOH give *acetyldehydrophenylalanylglycine* (*acetamidocinnamylglycine*), m.p. 194—195°, hydrogenated (Pd in MeOH-AcOH) to *acetyl-dl-phenylalanylglycine*, m.p. 178°. With this, papain-cysteine and NH_2Ph (citrate buffer) react only with the *l*-component, forming *acetyl-l-phenylalanylglycineanilide*, m.p. 208—209°, $[\alpha]_D^{25} +21.3^\circ$ in AcOH. Acetamidocinnamylglycine under similar conditions gives its *anilide*, m.p. 207—212°, α 0°. E. W. W.

Synthesis of umbellularic acid. P. C. GUHA and M. S. MUTHANNA (Current Sci., 1938, 6, 605).—Et α' -carbethoxy- α -isopropylsuccinate is converted into the α' -Br-derivative, b.p. 155—156°/3 mm., which with NPhEt_2 yields Et carbethoxyisopropylfumarate, b.p. 135—140°/3 mm. This readily adds 1 mol. of CH_2N_2 to yield Et 2-isopropylcyclopropane-1:1:2-tricarboxylate, b.p. 148—150°/3 mm., hydrolysed and decarboxylated by boiling 18% HCl to *trans*-umbellularic acid, m.p. 190—192°. L. S. T.

Shikimic acid and derivatives. II. Ammonium and substituted ammonium salts. H. H. LEI (J. Amer. Pharm. Assoc., 1938, 27, 393—396; cf. A., 1938, II, 25).—The NH_4 , NH_2Me , m.p. 163—164°, $\text{NH}_2\cdot\text{CH}_2\text{Ph}$, m.p. 195—196°, *ephedrine*, m.p. 162—163°, NH_2Ph , new m.p. 194—195°, *o*-toluidine, m.p. 178—180°, N_2H_4 , m.p. 147—148°, $\text{C}_5\text{H}_5\text{N}$, m.p. 184—185°, *quinine*, m.p. 221—222°, *quinidine*, m.p. 224—226°, *codeine*, m.p. 173—174° (sinters at 160°), and *strychnine*, m.p. 234—236° (sinters at 154°), salts are described (cf. Chen, A., 1930, 259). The *n*-propyl- and -amyl-amine salts were obtained as syrups. F. O. H.

Aminobenzoic esters of propanetriol [glycerol]. R. JACQUEMAIN and (Mlle.) G. DEVILLERS (Compt. rend., 1938, 207, 241—243).—The appropriate nitrobenzoates are reduced according to the technique described previously (cf. A., 1938, II, 255). The following are described: *glyceryl α -benzoate $\beta\gamma$ -di-*

aminobenzoate, m.p. 96° [*hydrochloride*, m.p. 173—176°; *hydrobromide*, m.p. 200° (decomp.)], *α -benzoate $\beta\gamma$ -di-*m*-aminobenzoate*, m.p. 88°, *α -benzoate $\beta\gamma$ -di-*p*-aminobenzoate*, m.p. 138° [*hydrochloride*, m.p. 214° (decomp.)]; *hydrobromide*, m.p. 210° (decomp.); *picrate*, decomp. $\sim 117^\circ$, *$\alpha\beta\gamma$ -tri-*o*-aminobenzoate*, m.p. 105° [*hydrochloride*, decomp. $\sim 150^\circ$; *hydrobromide*, m.p. 188°; *hydriodide*, unstable; *picrate*, m.p. 102°], *α -*o*-aminobenzoate $\beta\gamma$ -di-*p*-aminobenzoate*, m.p. 133°, *$\beta\gamma$ -di-*o*-aminobenzoate α -*m*-aminobenzoate*, m.p. 115°, *$\alpha\beta\gamma$ -tri-*m*-aminobenzoate*, m.p. 82°, *α -*m*-aminobenzoate $\beta\gamma$ -di-*p*-aminobenzoate*, m.p. 171° [*hydrochloride*, m.p. 200° (decomp.)], *$\beta\gamma$ -di-*o*-aminobenzoate α -*p*-aminobenzoate*, m.p. 109° [*hydrochloride*, m.p. 175—180° (decomp.)]; *hydrobromide*, decomp. $\sim 200^\circ$; *hydriodide*, decomp. $\sim 150^\circ$, and *$\alpha\beta\gamma$ -tri-*p*-aminobenzoate*, m.p. 168°. J. L. D.

Retardation of chemical reactions. VIII. Darkening of alkaline solutions of sodium salicylate.—See B., 1938, 977.

Esters of *p*-hydroxybenzoic acid as preservatives.—See B., 1938, 884.

Cyclisation of phenyl-1-naphthylmethane-*o*-carboxylic [*o*- α -naphthylmethylbenzoic] acid according to Fieser and Hershberg. R. SCHOLL and K. MEYER (Ber., 1938, 71, [B], 1482).—The cyclisation by small amounts of ZnCl_2 (Fieser *et al.*, A., 1937, II, 333) appears identical in principle with the use of small amounts of HI or HCl in boiling Ac_2O . H. W.

α - and β -Naphthoic acids. A. WAHL (Rev. Gén. Mat. Col., 1938, 42, 285—286).—Partly a more detailed account of work previously reviewed (A., 1938, II, 143). Comparison of a series of pyrazolone dyes indicates that derivatives of α -naphthylpyrazolone show the best fastness to light and washing. 5:1- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$, obtained by nitration of α - $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$ (I) and reduction of the 5- NO_2 -derivative (Me ester, m.p. 66°), is converted (diazo-method) into 5:1- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{CO}_2\text{H}$, m.p. 264—265° (Maquenne block), identical with the product obtained by direct bromination of (I). Corbellini and Barbaro's dibromoanthanthrone (A., 1933, 1054) is shown as follows to be the 2:7-derivative. *Me 5-bromo-1-naphthoate*, b.p. 210—212°/20 mm., m.p. 66°, with HNO_3 (*d* 1.45) at 15—20° yields the 8- NO_2 -derivative, m.p. 125—126°, reduction ($\text{Sn} + \text{HCl}$) then giving 5-bromonaphthasteryl. This is converted into 2:7-dibromoanthanthrone which has tinctorial properties similar to those of the commercial product obtained by bromination of anthanthrone. R. J. W. R.

Carboxylation of alkali-metal salts of phenols.—See B., 1938, 888.

Hydroxy-acids and unsaturated acids of the cyclopentanophenanthrene series.—See B., 1938, 982.

Determination of cholic acid. I. Fructose-hydrochloric acid method. Y. OHYAMA (J. Biochem. Japan, 1938, 27, 351—362).—The sample (≈ 0.1 —1.0 mg. of cholic acid) is mixed with fructose (approx. equal to wt. of cholic acid) in EtOH,

evaporated, and heated at 40° with conc. HCl (5 c.c.) for 20 min.; the red colour produced is compared with suitable standards or determined photometrically. The reaction is positive for tauro- and glyco-cholic and 7 : 12-dihydroxy-3-ketocholic acids but negative for cholesterol and some derivatives of cholic acid. The application of the method to blood, bile, and liver is described.

F. O. H.

Conversion of 7 : 12-dihydroxy-3-ketocholic acid into cholic acid in the toad. T. S. SHIN (J. Biochem. Japan, 1938, 27, 425—431).—Me triacetyleholate with N-KOH in MeOH yields 3-hydroxy-7 : 12-diacetoxycholic acid, m.p. 203—204°, oxidised (CrO₃ in AcOH) to 3-keto-7 : 12-diacetoxycholic acid, m.p. 197—198°, which is hydrolysed to 7 : 12-dihydroxy-3-ketocholic acid (I), m.p. 121—123°. Subcutaneous injection of the Na salt of (I) in 0.9% NaCl into toads is followed by urinary excretion of cholic acid. The action of (I) in hæmolysing erythrocytes (ox, goat) and accelerating hydrolysis of fats by lipase is < that of cholic acid.

F. O. H.

Colour reaction of deoxycholic acid. K. KAZIRO and T. SHIMADA (Z. physiol. Chem., 1938, 254, 57—60).—The acid, PhCHO, and 75% H₂SO₄ give a red colour, changed to green by addition of AcOH. The reaction is sp. for deoxycholic acid.

F. O. H.

Systematic degradation of chenodeoxycholic acid. T. ISHIMURA (J. Biochem. Japan, 1938, 27, 265—277).—Me chenodeoxycholate with MgMeI gives the corresponding dimethylcarbinol derivative, m.p. 178—179°, the diacetate (I), m.p. 153—157°, of which is oxidised (CrO₃) to the Ac₂ derivative, m.p. 213—214°, of norchenodeoxycholic acid [Me ester (+0.5H₂O), m.p. 85—87°], which, similarly treated, yields the dimethylcarbinol derivative, m.p. 182—183° [diacetate (II), m.p. 169—170°], and Ac₂ derivative, m.p. 226—227°, of bisnorchenodeoxycholic acid, C₂₂H₃₆O₄, m.p. 269—270°, [α]_D²⁵ -18.88° in EtOH [Me ester (III), m.p. 173—174°]. Oxidation (CrO₃) of (II) also gives a ketone diacetate, m.p. 189—190°, hydrolysed to a ketone, C₂₄H₄₀O₃, H₂O, m.p. 160—161° (sinters at 85°), [α]_D²⁵ +3.46° in EtOH. The diethylcarbinol (IV), m.p. 160—161°, from (III) and MgEtBr, acetylated and oxidised, affords 3 : 7-dihydroxyætiocolane-17-carboxylic acid, C₂₀H₃₂O₄, m.p. 165—166°. Oxidation (CrO₃) of (I) also gives a ketone diacetate, m.p. 132—133°, hydrolysed to a ketone, C₂₅H₄₂O₃, m.p. 175—176°, [α]_D²⁵ +9.01° in EtOH. 7-Hydroxypregnan-3-ol-20-one (+0.5H₂O), m.p. 170—172° (diacetate semicarbazone, m.p. 271—272°), is also formed during the oxidation of (IV) (as Ac derivative).

F. O. H.

Transformation of dehydroandrosterone into 3-hydroxy- Δ^5 -ætiocolanic acid; linking of the androsterone with the corticosterone group. A. BUTENANDT and J. SCHMIDT-THOMÉ (Ber., 1938, 71, [B], 1487—1492; cf. A., 1938, II, 236).—Dehydroandrosterone is converted by KCN in boiling EtOH-AcOH into the corresponding cyanohydrin, decomp. between about 210° and 250° according to the method of crystallisation and rapidity of heating (diacetate, m.p. 207—208°). Similarly dehydroandrosterone acetate

affords the two epimeric dehydroandrosterone cyanohydrin 3-acetates, (A), prisms, m.p. 195° (decomp.), or needles, m.p. 195° (decomp.) after softening at about 185° (temp. of decomp. depends greatly on external factors), and (B), m.p. 203—206° (decomp.). The mixture of epimerides is dehydrated by POCl₃ in boiling C₅H₅N to 17-cyano-3-acetoxy- Δ^5 :16-androstadiene (I), m.p. 210°, hydrolysed by NaOH-H₂O-EtOH at 180° to 3-hydroxy- Δ^5 :16-ætiocoladiene-17-carboxylic acid (II), m.p. 256° (decomp.) [acetate, m.p. 253—254° (decomp.) after softening at about 230°]. Partial hydrogenation of (II) leads to 3-hydroxy- Δ^5 -ætiocolanic acid.

H. W.

Condensation of malonanilic acid with aromatic aldehydes. R. K. MEHRA and K. C. PANDYA (Proc. Indian Acad. Sci., 1938, 7, A, 369—375).—Malonanilic acid (I), piperonal, and a C₅H₅N-piperidine mixture give, contrary to Ahluwalia *et al.* (cf. A., 1931, 1155), only piperonylidene malonanilic acid (II) and no 3 : 4-methylenedioxy cinnamanilide (III). At 60—70° and with longer heating, some (III) is formed. With C₅H₅N as condensing agent at 60°, only (II) is formed, but at 100° using either C₅H₅N or piperidine, (III) is the main product. Equimol. amounts of (I) and *o*-OH·C₆H₄·CHO at 100—104° afford coumarin-3-carboxylanilide in best yield when piperidine (0.15 mol.) is the condensing agent. Similarly, *m*- and *p*-OH·C₆H₄·CHO afford *m*- and *p*-hydroxycinnamanilide, m.p. 155—156° and 208°, respectively, and PhCHO affords cinnamanilide. (I) with *o*-NO₂·C₆H₄·CHO and C₅H₅N-piperidine (or either base separately) affords no *o*-nitrobenzylidenemalonanilic acid (cf. *loc. cit.*) but a mixture of a yellow, m.p. 190°, and a colourless, m.p. 172°, form of *o*-nitrocinnamanilide. Similarly, *m*- and *p*-NO₂·C₆H₄·CHO yield *m*- and *p*-nitrocinnamanilides, m.p. 194—195° and 208°, respectively. The yields obtained by using mixtures of C₅H₅N and piperidine, or of either base alone, are tabulated.

J. L. D.

Luminescence phenomena during the oxidation of luminol. H. THIELERT and P. PFEIFFER (Ber., 1938, 71, [B], 1399—1403).—The intensity of the luminescence during the oxidation of 3-aminophthalhydrazide (luminol) in presence of salicylaldehyde-ethylenedi-imine ferrichloride (I) is about one third of that observed in the presence of hæmin but the effect lasts much longer. Salicylaldehyde-*o*-phenylenedi-imine ferrichloride causes pale blue luminescence of relatively small intensity whereas salicylaldehydeanil ferrichloride is completely inactive. Fe^{III} salicylaldehyde-imine and -methylimine provoke only a faint luminescence which persists for a few min. whilst Fe^{III} salicylaldehyde is almost without effect.

The salt $\left[\text{Fe} \left(\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CO} > \text{C}_6\text{H}_4 \end{array} \right)_2 \right] \text{K}_4\text{H}_2\text{O}$ has a powerful but transient action. Fe phthalocyanine, [C₃₂H₁₆N₈Fe], 6NH₂Ph, is about as active as (I).

H. W.

Preparation of ammonium aurintricarboxylate.—See A., 1938, I, 473.

Catalyst in the Gattermann reaction. R. T. ARNOLD and J. SPRUNG (J. Amer. Chem. Soc., 1938, 60, 1699).—Zn(CN)₂ acts as catalyst for the Gattermann reaction only if it contains KCl or NaCl.

R. S. C.

Oxygen exchange reactions of benzaldehyde and some other substances. M. SENKUS and W. G. BROWN (J. Org. Chem., 1938, 2, 569—573).—By treatment with H₂O deficient in H₂¹⁸O it is shown that no exchange of O occurs with CO(NH₂)₂ or NaOAc at 25°. With citric acid exchange is catalysed by H₂SO₄. With PhCHO exchange is rapid and is catalysed by KOH or H₂SO₄. With (OMe·C₆H₄)₃C·OH, but not with BuⁿOH, exchange is catalysed by H₂SO₄. There is no exchange with CPh₂Me·OH alone or in presence of KOH. With alloxan exchange proceeds in stages.

R. S. C.

Synthesis of vanillin and other hydroxyaldehydes.—See B., 1938, 885.

Preferential demethylation of methoxyl ortho to a keto-group. W. A. HUTCHINS and T. S. WHEELER (Current Sci., 1938, 6, 604—605).—2 : 4 : 6-Trimethoxyacetophenone (5 g.), HI (*d* 1.7; 40 c.c.), and Ac₂O (40 c.c.) after keeping in the cold for 24 hr. and dilution with aq. NaHSO₃ give 2-hydroxy-4 : 6-dimethoxyacetophenone (80%); AlCl₃ gives a 60% yield). Alkoxy-derivatives of *o*-anisyl styryl ketones can also be preferentially demethylated to *o*-OH-compounds in this way.

L. S. T.

αβ-Ketols. K. VON AUWERS, H. PÖTZ, and W. NOLL (Annalen, 1938, 535, 219—251).—The structure of C₆H₄CHMe·OH (I) (A., 1937, II, 64) is confirmed by conversion of its oxime by PCl₅ into PhCN. A *p*-OH, however, causes COAr·CHMe·OH to be more stable than its isomeride, OH·CHAr·COMe. (I) gives a thiosemicarbazone, m.p. 143°. OH·CHPh·COMe gives the thiosemicarbazone, m.p. 206°, and in HCl-MeOH a 2 : 4-dinitrophenylhydrazone, m.p. 182—183° (cf. *loc. cit.* and Hey, A., 1930, 935), also obtained from (I). C₆H₄COMe gives a mono-, m.p. 175—176° (red; decomp.), and di-thiosemicarbazone, m.p. 218—220° (decomp.). EtCO₂Ph (best prepared from PhOH, EtCO₂H, and SOCl₂), b.p. 200—210°, or a mixture of EtCO₂H + PhOH gives, best with BF₃, *p*-hydroxypropionophenone [semicarbazone, m.p. 168—170°; *p*-nitro-, forms, m.p. 187—188° and >155°, and 2 : 4-dinitro-phenylhydrazone, m.p. 233°; *Me* ether, m.p. 173—174° (*p*-nitro-, m.p. 148—149°, and 2 : 4-dinitro-phenylhydrazone, m.p. 192—193°)]. With Br-AcOH followed by Br-CS₂ this gives the α : 3-Br₂-, m.p. 144—145°, and αα(β) : 3 : 5-Br₄-derivative, m.p. 79—80°, but in MeOH yields >90% of the 3 : 5-Br₂-derivative (II), new m.p. 114—115° [semicarbazone, m.p. 208—209°; *Ac* (III), m.p. 79.5—80.5°, and *Bz* derivative, m.p. 121—122°; *Me* ether (IV), m.p. 62—63° (semicarbazone, m.p. 193—194°)]. (II) and Br-CHCl₃ give the α : 3 : 5-Br₃-derivative, m.p. 162—163° (*Me* ether, m.p. 103°). With C₆H₁₁NO₂ and a little conc. HCl at 60—70° (III) gives 4 : 3 : 5-OH·C₆H₂Br₂·CO₂H and 3 : 5-dibromo-α-oximino-4-hydroxypropionophenone (V), m.p. 158—159.5°, which is obtained having m.p. 171—172° from (II) or by oximation of αβ-diketo-α-3 : 5-dibromo-4-hydroxyphenylpropane (VI), m.p. 118—119°. (VI) is ob-

tained from (V) by hot 18% HCl and gives the β-phenylhydrazone, m.p. 238—239° (*O*-Bz derivative, m.p. 153—154°), and β-semicarbazone, m.p. about 260° (decomp.); its *Me* ether, m.p. 107—108° (β-semicarbazone, m.p. 236°; β-phenylhydrazone, m.p. 229—230°), is obtained by hydrolysing the β-oxime, m.p. 149°, which is prepared from (IV) by C₆H₁₁NO₂ and HCl. α : 3 : 5-Tribromo-4-hydroxypropionophenone (VII) is converted, best by cold 2*N*-NaOH, into 3 : 5-dibromo-4-hydroxybenzoylmethylcarbinol [3 : 5-dibromo-α : 4-dihydroxypropionophenone] (VIII), m.p. (anhyd.) 112°, (+0.5C₆H₆) 93—94° [phenylhydrazone, m.p. 192°; impure *Bz*₂ derivative, an oil; semicarbazone, m.p. variable, 186—192°, hydrolysed by cold HNO₃ to (VIII); oxime, m.p. 162—163°, converted by PCl₅ in Et₂O into 4 : 3 : 5 : 1-OH·C₆H₂Br₂·CN]. (VIII) gives indefinite products with PCl₅, PBr₃, or SOCl₂; subsequent reduction by Zn dust and AcOH gives 4 : 3 : 5 : 1-OH·C₆H₂Br₂·CH₂·COMe (semicarbazone, m.p. 241°), isomerisation having occurred. CH₂N₂ (not MeI-NaOH) gives the 4-*Me* ether, b.p. 217—218°/16 mm., m.p. 77—79°, of (VIII); this gives, according to the conditions, its semicarbazone, m.p. 199—201°, or that of (VI), but gives only the phenylhydrazone of (VI). (VII) and KOAc in AcOH give the *Ac* derivative, m.p. 128°, of (VIII), the semicarbazone, m.p. 177°, of which is also obtained from the *Ac*₂ derivative, m.p. 89°, of (VIII). *p*-Hydroxyphenylacetone, b.p. 178—180°/13 mm. (lit., m.p. 35.5°), is best obtained from its *Me* ether by AlBr₃ in hot C₆H₆; it gives oily 3 : 5-Br₂- and α : 3 : 5-Br₃-derivatives. Ph α-bromopropionate (A., 1917, i, 37), b.p. 123—126°/10 mm., with AlCl₃ gives α-bromo-*p*- (IX), m.p. 95° (lit., 81°), and -*o*-hydroxypropionophenone, m.p. 36.5—37° (lit., 32°), b.p. 138—140°/12 mm. (identified by dehalogenation). Ph α-chloropropionate, b.p. 117—120°/14 mm., and α-chloro-*p*- (X), m.p. 81.5°, and -*o*-hydroxypropionophenone, b.p. 126—128°/10 mm., are similarly prepared. *o*-Hydroxypropionophenonesemicarbazone (?) has m.p. 206.5—207°. (IX) or, less well, (X) and 2*N*-NaOH give *p*-hydroxybenzoylmethylcarbinol [α : 4-dihydroxypropionophenone] (XI), m.p. 141° [oxime, m.p. 173.5°, and (?) a stereoisomeride thereof], which yields the disemicarbazone, m.p. 256—257° (decomp.), and 2 : 4-dinitrophenyllosazone, decomp. 279—280° (sinters at about 260°), of αβ-diketo-α-*p*-hydroxyphenylpropane, and with Br gives (VIII). *p*-OMe·C₆H₄·CO·CHMeBr and KOAc in AcOH give α-acetoxy-*p*-methoxypropionophenone, m.p. 72—73°, hydrolysed by BaCO₃ to *p*-anisoylmethylcarbinol [α-hydroxy-*p*-methoxypropionophenone] (XII), b.p. 158—160°/9.5 mm., obtained also in one step by 2*N*-NaOH. (XII) and PCl₅ give a product, reduced by Zn-AcOH to *p*-OMe·C₆H₄·COEt. (XII) gives its semicarbazone, m.p. 200°, and the disemicarbazone, m.p. 246°, of αβ-diketo-α-*p*-anisylpropane (XIII); it affords also the impure 2 : 4-dinitrophenylhydrazone, m.p. 258° after sintering, of (XIII). The structures assigned to (XI) and (XII) are supported by the large exaltation of *ν*.

R. S. C.

Friedel-Crafts reaction with diethers of resorcinol. D. C. MOTWANI, V. V. BODANI, and T. S. WHEELER (Current Sci., 1938, 6, 604).—Cinnamoylation of *m*-C₆H₄(OAlk)₂ occurs at position 4 to give 1 : 3 : 4-(OAlk)₂C₆H₃·CO·CH·CHPh identical with

those obtained from *OO*-dialkylresacetophenones and PhCHO (cf. A., 1927, 154). The styryl ketones from 2-acetyl-*OO*-dialkylresorcinols and PhCHO differ from those described by Simonis (*loc. cit.*). L. S. T.

Preparation and properties of an ene-diol. β -Mesityl- α -phenylacetylene glycol [γ -keto- α -phenyl- γ -mesityl- Δ^{α} -propene- $\alpha\beta$ -diol]. R. P. BARNES and L. S. GREEN (J. Amer. Chem. Soc., 1938, 60, 1549—1553).—An open-chain ene-diol is prepared, the relative stability being due to suitable activating groups. p -C₆H₄Br·COMe (I), HCO₂Et, and NaOEt in C₆H₆ give ω -hydroxymethylene- p -bromoacetophenone (II), m.p. 71° (67% enolic), yielding Ac, m.p. 125°, and Bz derivatives, m.p. 112°, which decolorise Br and KMnO₄, give only slowly a colour with FeCl₃-EtOH, and are hydrolysed by HCl-EtOH to (I) and EtOAc or EtOBz, respectively. With cold Br-CHCl₃ the Na derivative of (II) gives the α -Br-derivative, p -C₆H₄Br·CO·CBr·CH·OH, m.p. 112° [100% enolic; red FeCl₃ colour; reduced by HI to (II)], which is resinified by hot KOAc-AcOH. HCl-EtOH hydrolyses (II) to (I) and HCO₂Et. 2:4:6-

C₆H₂Me₃·CO·C(OH)·CHPh (III) and Br-Et₂O give α -bromo- α -phenyl- γ -mesitylpropane- $\beta\gamma$ -dione, an oil [24% enolic; reduced to (III) by HI], which with hot KOAc-AcOH gives α -acetoxy- α -phenyl- γ -mesityl- Δ^{α} -propen- γ -one (IV), m.p. 71° (100% enolic; unchanged by hot HCl- or H₂SO₄-EtOH; cleaved by alkaline H₂O₂ to EtOAc, BzOH, and C₆H₂Me₃·CO₂H), converted by hot AcCl into $\alpha\beta$ -diacetoxy- α -phenyl- γ -mesityl- Δ^{α} -propen- γ -one, m.p. 131° (no FeCl₃ colour; decolorises KMnO₄ and Br). Both OAc-compounds are converted by cold, conc. H₂SO₄ into γ -keto- α -phenyl- γ -mesityl- Δ^{α} -propene- $\alpha\beta$ -diol (V), m.p. 79—80° (greenish-blue FeCl₃ colour; 37% ene-diol). When kept in air or Et₂O or treated with H₂SO₄-EtOH, (V) gives α -phenyl- γ -mesitylpropane- $\alpha\beta\gamma$ -trione, m.p. 94°, α -phenyl- β -mesitylgllyoxal (VI), m.p. 134°, H₂O₂, and CO₂. (VI) is also formed from (V) by Br-CHCl₃ or FeCl₃-EtOH, and from (IV) by Br-CHCl₃. Alkaline H₂O₂ oxidises (VI) to BzOH and C₆H₂Me₃·CO₂H.

R. S. C.

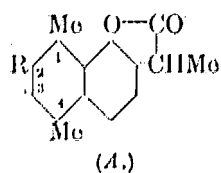
Deformation of valency angles. Structure and absorption of derivatives of oximes. (MME.) RAMART-LUCAS and J. HOCH (Bull. Soc. chim., 1938, [v], 5, 987—1010).—Measurements of the absorption of derivatives of oximes (*O* and *N* compounds) which cannot behave as tautomerides, and the structures of which have been determined in part by optical and in part by chemical methods, confirm the view that oximes exist not only in the "oxime" and "isoxime" forms but also in a peculiar form ("transparent" form) in which the union between the functional group and the remainder of the mol. is nil. The spectra of derivatives of CHPh·N·OH, 3:4-CH₂O₂:C₆H₃·CH·N·OH, CPhEt·N·OH, CPh₂·N·OH, p -OMe·C₆H₄·C(N·OH)·C₆H₄Me- p' and of CAlk₃·CPh·N·OH are recorded. *O*-CH₂Ph derivatives are obtained by the action of NH₂·O·CH₂Ph on aldehydes or ketones or on ketimines or from the oxime, NaOEt, and CH₂PhCl in EtOH. CH₂Ph·NH·OH reacts readily with aldehydes but appears indifferent to ketones or their acetals although the change occurs with ketimines. The following are new or amended:

O-, m.p. 55°, and *N*-benzyl-3:4-methylenedioxybenzaloxime, m.p. 121°; propiophenoneoxime CH₂Ph ether, b.p. 195°/22 mm.; *O*-benzylbenzophenoneoxime, m.p. 61°, and *N*-benzhydrylbenzaloxime, m.p. 166° (hydrolysed by hot dil. HCl to PhCHO and CHPh·NH·OH), formed from CPh₂·N·OH, NaOEt, and CH₂PhCl [thus CPh₂·NO·CH₂Ph (not isolated) \rightarrow CHPh₂·NO·CHPh]; *O*-benzyl-4-methoxy-4'-methylbenzophenoneoximes (*cis*- and *trans*-isomerides), m.p. 71° and 115°, respectively; *O*-benzyl-3:4-methylenedioxybenzophenoneoxime, m.p. 84°; Ph Bu^v ketoxime CH₂Ph ether, m.p. 41°; Ph β -methyl- β -hexyl ketoxime CH₂Ph ether, b.p. 200°/15 mm., reduced (Na and EtOH) to α -amino- α -phenyl- $\beta\beta$ -dimethylhexane, b.p. 145—146°/12 mm. (corresponding phenylcarbamide, m.p. 140°), and CH₂Ph·OH; Ph α -phenyl- β -methyl- β -propyl ketoxime CH₂Ph ether, m.p. 82°; 2:2-dimethylindanoneoxime CH₂Ph ether, b.p. 200°/13 mm.; indanoneoxime CH₂Ph ether, b.p. 171—173°/1 mm., m.p. 29°, and an isomeride, m.p. 142—143°; 3:4-methylenedioxybenzophenone, m.p. 56°; *p*-tolyl *p*-anisyl ketimine, m.p. 61°; 3:4-methylenedioxybenzophenoneimine, b.p. 210—211°/11 mm. H. W.

Action of mixed organo-magnesium compounds on *N*-acyl-*N'*-phenylhydrazines. P. GRAMMATICAKIS (Compt. rend., 1938, 207, 239—241; cf. A., 1937, II, 248, 287).—Prolonged heating of *N*-formyl-*N'*-phenylhydrazine with a large excess of MgPhBr at 116—120° affords mainly COPh₂ together with small amounts of CPh₂·N·NHPh (I) and CPh₂·NPh (II). NHAc·NHPh similarly treated affords mainly 2-phenylindole and small amounts of CPhMe·N·NHPh and COPhMe. NHBz·NHPh similarly affords (I), (II), NH·CPh₂, and COPh₂. In every case some NH₂Ph and NHPh·NH₂ are formed. The formation of these products can be explained by assuming that the *N*-acyl-*N'*-phenylhydrazines react as OH·CR·N·NHPh. J. L. D.

Nickel (Ni^{II}) salts of acyloinoximes and of oximinoketones. L. MALATESTA (Gazzetta, 1938, 68, 319—323).—Ni dibenzoinoxime (A., 1935, 981) in KOH-EtOH with Ni(OAc)₂ gives the complex K[NiH(C₁₄H₁₁O₂N)₂], diamagnetic. Similarly Ni piperoin- and anisoin-oxime, paramagnetic, give diamagnetic *K* complexes. The Ni derivatives of furoin- and salicylal-oxime (*K* complex), of oximinobenzoylacetone and -acetophenone (*K* complex), and of α -benzildioxime are prepared, and γ and μ tabulated; all these, including *K* compounds, are paramagnetic. Structures are discussed. E. W. W.

Quinols. I. Hyposantonylquinol and tetrahydronaphthalencquinol. Y. ASAHINA and T. MOMOSE (Ber., 1938, 71, [B], 1421—1428).—Gradual addition of conc. HNO₃-conc. H₂SO₄ to hyposantonin



in AcOH at 20—30° gives 2-nitrohyposantonin (I) (A; R = NO₂), m.p. 183°, [α]_D²⁵ -67.6° in CHCl₃, also obtained similarly from isohyposantonin. Its constitution is established by its conversion (Zn dust and NH₄Cl in boiling 50% PhOH) through 2-aminohyposantonin (II), m.p. 193°, [α]_D²⁵ -165.7° in CHCl₃ [hydrochloride, m.p. 118—119°

(decomp.), into *l*-desmotroposantonin, m.p. 198°, $[\alpha]_D^{25}$ -140.0° in abs. EtOH (acetate, m.p. 154°). Reduction (Pd-C in EtOH) of (I) yields *aminopyrosantonous acid*, m.p. 246° [hydrochloride, m.p. 212—213° (decomp.), $[\alpha]_D^{25} +62.5^\circ$ in HCl], also obtained by hydrogenation of (II) and converted by HCl and NaNO₂ into *d*-santonous acid, m.p. 182—183°, $[\alpha]_D^{25} +75.0^\circ$ in abs. EtOH (*Me* ester, m.p. 86°). Conc. H₂SO₄-conc. HNO₃ at 35—40° convert (I) into *dinitrohyposantonin*, m.p. 209°, $[\alpha]_D^{25} -62.0^\circ$ in CHCl₃, whence (Pd-C in EtOH at 25°) *diaminohyposantonous acid*, m.p. 218—219°, $[\alpha]_D^{25} +79.1^\circ$ in 1% HCl. Attempts reduce to (I) in neutral solution to 2-hydroxylaminosantonin were unsuccessful but (II) is transformed by Caro's acid into 2-nitrosohyposantonin, m.p. 146° (decomp.), $[\alpha]_D^{18} -185.8^\circ$ in CHCl₃, which when warmed with Na₂SO₃ gives a solution which strongly reduces Fehling's solution and when directly subjected to Bamberger's reaction affords *hyposantonylquinol* (structure: A., 1938, II, 284), m.p. 222—223°, $[\alpha]_D^{24} +324.8^\circ$ in abs. EtOH (*oxime*, m.p. 188°; *mono*-, m.p. 204°, and *di*-, m.p. 200—201°, -acetate), which is an anthelmintic and possibly the physiologically active derivative of santonin. 6-Nitro-1:2:3:4-tetrahydronaphthalene when treated with Zn dust and NH₄Cl in EtOH and then digested with dil. H₂SO₄ at 60—70° gives 10-hydroxy-2-keto-2:5:6:7:8:10-hexahydronaphthalene, m.p. 124—125°, which like its acetate, m.p. 81°, is a powerful anthelmintic. It is converted by Ac₂O-H₂SO₄ into the *diacetate*, m.p. 188°, of 5:8-dihydroxy-1:2:3:4-tetrahydronaphthalene, m.p. 179—180°. H. W.

New synthetic route to polycyclic hydroaromatic compounds. Synthesis of 2:3-benzodicyclo-[0:3:3]- Δ^2 -octene [and of 8-ketohexahydropentanthyrene ketone]. N. N. CHATTERJEE (J. Indian Chem. Soc., 1938, 15, 211—216).—OH-CHPh-CN with CN-CHNa-CO₂Et, followed by CH₂Cl-CH₂-CO₂Et yields *Et*₂ $\alpha\beta$ -dicyano- α -phenyl-*n*-butane- $\beta\delta$ -dicarboxylate, m.p. 81°, b.p. 218—222°/5 mm., hydrolysed and decarboxylated to α -phenyl-*n*-butane- $\alpha\beta\delta$ -tricarboxylic acid, m.p. 185° (decomp.), the *Et*₃ ester, b.p. 187—194°/5 mm., of which with Na in C₆H₆ gives *Et*₂ 2-phenylcyclopentanone-3:5-dicarboxylate, b.p. 184—192°/5 mm., hydrolysed and decarboxylated to 2-phenylcyclopentanone-3-carboxylic acid (I), m.p. 114—115°. This is reduced (Zn-Hg + HCl) to 2-phenylcyclopentane-1-carboxylic acid, b.p. 185—190°/10 mm., the chloride of which is cyclised (AlCl₃ in CS₂) to 4-keto-2:3-benzodicyclo-[0:3:3]- Δ^2 -octene, $\text{CO}-\text{CH}-\text{CH}_2 > \text{CH}_2$ (II), b.p. 127—132°/10 mm. (*semicarbazone*, m.p. 170°), reduced (Zn-Hg + HCl) to the hydrocarbon [(II); CO = CH₂], b.p. 118—124°/9 mm. The *Et* ester, m.p. 60° (*semicarbazone*, m.p. 173°), of (I) with Zn and CH₂Br-CO₂Et in C₆H₆ gives *Et*₂ 2-phenylcyclopentanol-3-carboxylate-1-acetate, b.p. 190—197°/6 mm., dehydrated (SOCl₂-Et₂O-C₅H₅N) to the Δ^1 -cyclopentene ester, b.p. 184°/5 mm., reduced (H₂, PtO₂, EtOH) to the *Et*₂ ester, b.p. 175—177°/5 mm., of 2-phenylcyclopentane-3-carboxylic-1-acetic acid, m.p. 170—173°. The chloride of this is cyclised (AlCl₃ in CS₂) to 8-ketohexahydropentanthyrene ketone (?). A. Li.

Adreno-genital syndrome. I. Isolation of 3(α)-hydroxyaetiocholan-17-one, 3(β)-hydroxyaetioallocholan-17-one (isoandrosterone), and a new triol from the urine of a woman with an adrenal hyperplasia. G. C. BUTLER and G. F. MARRIAN (J. Biol. Chem., 1938, 124, 237—247, and Nature, 1938, 142, 400; cf. A., 1937, III, 361).—The unhydrolysed urine of a woman with an adrenal hyperplasia and symptoms of virilism contained, in the ketonic portion of the neutral Et₂O-sol. fraction, 3(α)-hydroxyaetiocholan-17-one [(β) is used to denote that the C₃-OH group is in cholesterol-like relation to C₁₀-Me, and (α) to denote epimeric configuration as in the bile acids and androsterone], not digitonin-precipitable, and 3(β)-hydroxyaetioallocholan-17-one (isoandrosterone), digitonin-precipitable. These compounds (cf. A., 1934, 1221) have not previously been isolated directly from natural sources. The non-ketonic portion contains pregnane-3(α):17:20-triol (?) [Ac derivative, new m.p. 150—151° (cf. A., 1937, III, 361)], not digitonin-precipitable, and a triol, C₂₁H₃₆O₃, m.p. 210—212°, precipitable, which is probably a pregnane- [or allopregnane]-3(β):17:20-triol; with Pb(OAc)₄ it gives an aldehyde or ketone, and a product, m.p. 144—146°. E. W. W.

Enol ethers of steroid ketones. E. SCHWENK, G. FLEISCHER, and B. WHITMAN (J. Amer. Chem. Soc., 1938, 60, 1702—1703).—With CH(OEt)₃, a little HCO₂H, and a drop of H₂SO₄ at 50° cholestenone, and testosterone benzoate and propionate give the enol *Et* ethers, m.p. 83.5—85° (clear at 95°), $[\alpha] -96^\circ$ in C₅H₅N, m.p. 181—192° (softens at 175°), $[\alpha] -67.5^\circ$ in C₅H₅N, and (I), m.p. 143—150°, $[\alpha] -140^\circ$ in CHCl₃, respectively. In CHCl₃ (not C₅H₅N) the ethers are rapidly hydrolysed to the ketone, probably by adventitious traces of HCl. KOH-EtOH hydrolyses the ester grouping of (I) without affecting the OEt. Since $[\alpha]$ are negative, the ethylenic linkings are in different rings (A and B). R. S. C.

Reduction of Δ^5 -unsaturated 3-keto-derivatives of the cyclopentanohydrophenanthrene series.—See B., 1938, 982.

Synthesis of 3:4-methylenedioxyphenylglyoxal. S. KAWAI and K. ASHINO (Bull. Chem. Soc. Japan, 1938, 13, 480—481).—Homopiperonal and SeO₂ in hot EtOH give 3:4-methylenedioxyphenylglyoxal, an oil (*phenylhydrazone*, m.p. 140°; *quinoxaline* derivative, m.p. 167.5°), isolated as *Et semiacetal*, m.p. 107°. R. S. C.

Modified Gattermann reaction. Synthesis of hydroxyaldehydophenyl ketones. H. A. SHAH and R. C. SHAH (Nature, 1938, 142, 163).—Polyhydric phenolic ketones give aldehydes in high yield by a modified Gattermann reaction (A., 1937, II, 21), the CHO entering the 2-position in the resorcinol nucleus when possible. Resacetophenone, orsacetophenone, 2-acetylresorcinol, phloracetophenone, and 2:4-dihydroxybenzophenone give 2:4-dihydroxy-3-, 2:4-dihydroxy-6-methyl-3-, 2:6-dihydroxy-5-, 2:4:6-trihydroxy-3-aldehydoacetophenone, and 2:4-dihydroxy-3-aldehydobenzophenone, respectively. The entry of CHO into the 3-position of, e.g., 2:4:1-(OH)₂C₆H₃·COMe may be due to chelation between

OH and Ac stabilising the double linkings in the C_6H_6 ring.

L. S. T.

Synthesis of $\alpha\beta$ -diferulyl- $[\alpha\beta$ -di-(4-hydroxy-3-methoxycinnamoyl)]-ethane (a homologue of curcumin). W. LAMPE and J. SWIDERSKI (Rocz. Chem., 1938, 18, 120—124).—Sodio-*O*-carbomethoxyferulylacetone and I in Et_2O (12 hr. at room temp.) yield $\alpha\beta$ -di(carbomethoxyferulyl)- $\alpha\beta$ -diacetyethane, m.p. 220°, which with boiling AcOH (6 hr.) gives $\alpha\beta$ -di-(carbomethoxyferulyl)ethane, m.p. 159—160°. This and 10% KOH at 50° (1.5 hr.) in H_2 give $\alpha\beta$ -diferulylethane (I), m.p. 190—191°, together with its enolic modification, m.p. 179—180°. (I) dyes cotton a pale yellow, and does not give the curcumin reaction with H_3BO_3 . The Cu salt, m.p. 158° (decomp.), of Et *O*-carbomethoxyferulylacetate is described. R. T.

Synthesis of 3-benzoyl-2-phenylcyclopentanone. R. C. FUSON, R. JOHNSON, and W. COLE (J. Amer. Chem. Soc., 1938, 60, 1594—1595).—3-Benzoyl-2-phenylcyclopentanone (I) (A., 1934, 1005) is synthesised. The crude additive product from cyclopentene, $BzCl$, and $AlCl_3$ in CS_2 at -5° , with $NPhEt_2$ at 180° gives 1-benzoylcyclopentene, b.p. 119—122°/3 mm., which with NaOMe and *p*- $C_6H_4Cl\cdot CHO$ gives 1-benzoyl-3-*p*-chlorobenzylidenecyclopentene, m.p. 118°. $MgPhBr$ converts this into 1-benzoyl-2-phenyl-3-*p*-chlorobenzylidenecyclopentane, m.p. 171° (corr.) (oxime, m.p. 115—120°), converted by NaOH-MeOH, best with a little *p*- $C_6H_4Cl\cdot CHO$, into an isomeride, m.p. 178° (corr.). Ozonisation of either form in AcOH gives (I) (oxime, m.p. 222—224°). 3-Benzoyl-2-phenyl-5-*p*-chlorobenzylidenecyclopentanone is prepared by heating (I) with *p*- $C_6H_4Cl\cdot CHO$ and NaOH-MeOH. R. S. C.

Preparation of polyhydroxy-derivatives in the steroid group; addition of hydrogen peroxide to $\alpha\beta$ -unsaturated ketones. A. BUTENANDT and H. WOLZ (Ber., 1938, 71, [B], 1483—1487).— $\alpha\beta$ -Dihydroxyketones are obtained from unsaturated ketones and H_2O_2 in Et_2O or C_6H_6 containing a little OsO_4 at room temp. Thus cholestenone gives cholestane-4:5-diol-3-one, m.p. 206—208°, $[\alpha]_D^{25} +43.8^\circ$ in $CHCl_3$ (4-monoacetate, m.p. 225—227°). Δ^1 -Cholestenone yields cholestane-1:2-diol-3-one, m.p. 186—188°, whilst cholestane-4:5-diol-3:6-dione, m.p. 243—245° after gradual decomp. at $>200^\circ$, $[\alpha]_D^{25} -15.6^\circ$ in $CHCl_3$ (4-monoacetate, m.p. 224—226°), is obtained from Δ^4 -cholestene-3:6-dione. Progesterone affords pregnane-4:5-diol-3:20-dione, m.p. 249—250° (decomp.), $[\alpha]_D^{25} +104.5^\circ$ in $CHCl_3$ (4-monoacetate, m.p. 223—225°), and testosterone acetate yields androstane-4:5:17-triol-3-one 17-monoacetate, m.p. 185—188°, $[\alpha]_D^{25} +35.7^\circ$ in $CHCl_3$ [corresponding 4:17-diacetate, m.p. 220—222° (decomp.)]. Addition of 2 OH to the double linking vicinal to CO almost nullifies the physiological activity. H. W.

Sterols. XXXVI. Ketones from mares' pregnancy urine. R. E. MARKER, E. J. LAWSON, E. L. WITTLE, and H. M. CROOKS (J. Amer. Chem. Soc., 1938, 60, 1559—1561; cf., A., 1938, II, 362).—The ketones, separated by Girard's reagent from the non-phenolic portion of mares' pregnancy urine, give mixed semicarbazone fractions, each contain-

ing at least one ketone and OH-ketone. They yield Heard's ketone, m.p. 252° (A., 1938, II, 146) (mol. wt. 672; probably composed of two sterols united by their O; semicarbazone, m.p. 300°), *allopregnanedione*, m.p. 196—200°, *pregnanedione*, m.p. 118°, *allopregnan-3(β)-ol-20-one* (I), m.p. 193°, *uran-11-ol-3-one* (II), m.p. 165° [gelatinous semicarbazone, m.p. 250° (decomp.)], and a ketone, m.p. 115—120° (no digitonide). The structure of (II) follows from its giving the Zimmermann reaction (CO at position 3), not giving a H succinate (inert OH at C_{11}), and oxidation to uranedione, m.p. 175—176°. Isolation of (I) supports the proposed scheme of reduction of progesterone. Other ketones were present in mares' pregnancy urine, but were not purified. R. S. C.

Carotenoids of invertebrates. E. LEDERER (Bull. Soc. Chim. biol., 1938, 20, 567—610).—Astacine (1) has been obtained from the ascidians *Dendrodoa grossularia*, van Beneden, and *Halocynthia papillosa* which also contains a xanthophyll, *cynthia-xanthine*, m.p. 188—190° (shows absorption bands in CS_2 at 517, 483, and 451 mμ.). The genital organs of *Pecten maximus* contain a xanthophyll termed *pectenoxanthine*, $C_{40}H_{54}O_3$, which contains 11 double linkings, 2 OH, and one CO and shows absorption bands in CS_2 at 518, 586, and 452 mμ. *Calanus finmarchicus* contains (I). The genital glands of *Strongylocentrotus lividus* contain *echinenone*, $C_{40}H_{58}O$, m.p. 192—193°, which is a ketone and behaves like provitamin-A and shows a strong absorption band in CS_2 at 488 mμ.; it contains half of the mol. of β-carotene. *Pentaxanthine*, $C_{40}H_{56}O_5$, m.p. 209—210°, which is obtained from the mesentery of *S. lividus*, is the only xanthophyll known which contains 5 O; it has 11 double linkings, 3 OH, and probably 2 CO and shows absorption bands in CS_2 at 506, 474, and 444 mμ. The carotenoids of the lower animals are derived from the plant carotenoids. P. G. M.

Sterols. XXXIX. Reduction of uranetrione. R. E. MARKER, E. L. WITTLE, and T. S. OAKWOOD (J. Amer. Chem. Soc., 1938, 60, 1567—1569).— PtO_2 -hydrogenation of uranetrione in $EtOH-Et_2O$ at 25°/3 atm. proceeds homogeneously at C_{11} and C_{20} , the products being a substance giving a digitonide and *urane-3(α):11(β):20(β)-triol* (I), m.p. 255° (*triacetate*, m.p. 192°, indifferent to H_2-PtO_2 in AcOH at 85° and CrO_3-AcOH at 25°; no digitonide). In AcOH at 85°/3 atm. (I), *urane-3:11-diol* (II), m.p. 215° (*loc. cit.*); and other products are obtained. Partial hydrogenation in $EtOH$ gives an *uranoldione*, $C_{21}H_{32}O_3$, m.p. 225° (digitonide, proving a β-OH at C_{20} ; *acetate*, m.p. 250°). C_{20} is thus the first point of reduction. Formation of *urane-* and *pregnanedione* (A., 1938, II, 277) involves partial elimination of CO at C_{20} [to give (II)] and at C_{11} [with inversion at C_{20} to form *pregnanediol*]. The *uranetriol* previously (*loc. cit.*) isolated is the 3(α):11(β):20(α)-triol. (II) is only slightly epimerised by Na-xylene. R. S. C.

Mechanism of the pyrocatechol-tyrosinase reactions. H. WAGREICH and J. M. NELSON (J. Amer. Chem. Soc., 1938, 60, 1545—1548).—In the presence of tyrosinase (1) at p_H 6.2 pyrocatechol (II)

absorbs 2 O. After absorption of 1 atom 98% of *o*-benzoquinone (III) is present. If (II) is oxidised to (III) by $\text{Ce}(\text{SO}_4)_2$ at p_{H} 4.4 or $\text{K}_3\text{Fe}(\text{CN})_6$ at p_{H} 7.7, no O_2 is subsequently absorbed in absence of (I); in presence of (I) the rate of absorption of O_2 is the greater the longer is the time elapsing before addition of the (I), but the total amount absorbed is always approx. the same. Beyond a certain limit, nevertheless, a longer time interval does not increase the rate of absorption. This indicates that the (III) formed decomposes to a new oxidisable substance, which comes eventually into equilibrium with it. If (III) is formed by means of $\text{Ce}(\text{SO}_4)_2$ at p_{H} 4.8 or 4.5 and is then allowed mostly to decompose, addition of (I) leads to re-formation of (III) in amount indicating that 1 mol. of (II) is formed by each 2 mols. of (III) decomposed. Therefore, the following reactions are postulated: (a) slow, $(\text{III}) + \text{H}_2\text{O} \rightarrow 1:2:4\text{-C}_6\text{H}_3(\text{OH})_3$ (IV); (b) fast, $(\text{III}) + (\text{IV}) \rightarrow (\text{II}) + 2\text{-hydroxy-}p\text{- or 4-hydroxy-}o\text{-benzoquinone}$ (V); (c) fast, polymerisation of (V). Reaction (c) is indicated also by formation of humic material from aq. solutions of (III). Reactions (a) and (b) probably occur only when dil. solutions of (III) are rapidly oxidised at p_{H} 4–6, as the disappearance of (III) is a first-order reaction only in dil. solution and is accelerated by addition of (II). R. S. C.

Mechanism of the pyrocatechol-tyrosinase reaction. II. **Hydrogen peroxide question.** C. R. DAWSON and B. J. LUDWIG (J. Amer. Chem. Soc., 1938, 60, 1617–1621; cf. A., 1938, III, 338).—Tyrosinase (I), obtained from *Psalliotia campestris*, has no peroxidase and negligible catalase activity. At p_{H} 4.2–6.6 in presence of (I) pyrocatechol (II) rapidly absorbs O_2 to give a substance absorbing 2 I and, therefore, either 1 mol. of *o*-benzoquinone (III) or an equiv. mixture of $(\text{III}) + \text{H}_2\text{O}_2$; between p_{H} 4.2 and 6.6 the stability of (III) is independant of the p_{H} , but in more alkaline solution decomp. is faster. Addition of H_2O_2 has no effect on the oxidation of (II) under the influence of (I) at p_{H} 4.1, at which p_{H} H_2O_2 is without effect on (III). Addition of catalase has no effect on the oxidation of (II) induced by (I) at p_{H} 4.1–6.7. It is concluded that H_2O_2 plays no part in the oxidation of (II) to (III). R. S. C.

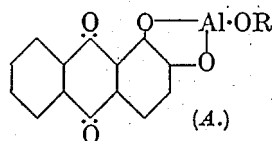
Potentiometric and magnetometric study of the duroquinone system. L. MICHAELIS, M. P. SCHUBERT, R. K. REBER, J. A. KUCK, and S. GRANICK (J. Amer. Chem. Soc., 1938, 60, 1678–1683).—Potentiometric, reductive titration and the magnetic susceptibility during reduction of duroquinone indicate formation of a brown, paramagnetic, free semiquinone, $\text{O}^-\cdot\text{C}_6\text{Me}_4\cdot\text{O}^-$, the amount of which present in the equilibrium mixture depends on the p_{H} and is a max. (about 50%) at p_{H} 13. No quinhydrone is formed, owing to steric hindrance by the Me. Quinhydrones are formulated $\text{C}_6\text{H}_4\begin{smallmatrix} \text{O} & \text{H} & \text{O} \\ \diagdown & & / \\ \text{O} & \text{H} & \text{O} \end{smallmatrix} \text{C}_6\text{H}_4$, etc. R. S. C.

Silicon as reducing agent in organic chemistry. A. ROLLETT and H. GANTZ (Monatsh., 1938, 72, 63–64).—Si + aq. NaOH at 100° (bath) is a weak and slow-acting reducing agent. It does not attack $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ or $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, but it reduces

indigotin, anthraquinone, 1:5-dinitroanthraquinone (low yield of 1:5-nitroamino-compound), and also azo-dyes (fission at N:N). A. T. P.

Constitution and reactivity. XXI. Substantivity of derivatives of 1- and 2-aminoanthraquinone. K. LAUER and L. S. YEN (J. pr. Chem., 1938, [ii], 151, 49–60).—Examination of the behaviour towards cotton cellulose of 1- and 2-acylaminoanthraquinones (acyl = Ac, $\text{CH}_2\text{Cl}\cdot\text{CO}$, $\text{CCl}_3\cdot\text{CO}$, Pr^nCO , Bz, *o*-, *m*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}$, *o*- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}$, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$, and $\text{CHPh}\cdot\text{CH}\cdot\text{CO}$) shows that substantivity is conditioned by keto-enolic tautomerism of the acylamino-group. The position of the equilibrium influences the rapidity of the completion of the dyeing but not the substantivity. The quantity of utilised dye alters with change in the acyl residue. The latter behaves as a substituent which affects the final union by its residual valencies; these can have a positive or negative action on substantivity according to the spatial position and polar character. H. W.

Alizarates. II. R. HALLER (Helv. Chim. Acta, 1938, 21, 844–853; cf. B., 1938, 637).—Alizarin-red which has not been subjected to the second treatment with oil and to steaming is decidedly altered by FeCl_3 , FeSO_4 , Sn^{++} , UO_2^{++} , Cr^{+++} , and Cu^{++} whereas finished alizarin-red remains unaffected. The effect does not depend on the presence of excess of alizarin (I). The same reactivity is shown by Ca and Al alizarate separately. The reaction is definitely ionic. Samples treated with a 20% solution of Turkey-red oil and then steamed have been impregnated with solutions of Al^{+++} , Fe^{+++} , Cr^{+++} , UO_2^{++} , Cu^{++} , Zn^{++} , Ni^{++} , Co^{++} , Ca^{++} , and Sn^{++} . The properties of the lakes and their behaviour towards MeOH are recorded. When treated with boiling solutions of other metallic salts, it is found that Fe^{+++} affects the colour of all other metallic mordants. Al^{+++} is without influence. Cu^{++} has little influence on the unsteamed pigments, which are very greatly altered by UO_2^{++} . Sn^{++} changes the colours due to Cu^{++} , Co^{++} , Ni^{++} , and Zn^{++} . Cr^{+++} has no effect on the Al^{+++} or Sn^{++} lakes; its effect in other cases could not be examined by reason of the similarity of colour. Anthrapurpurin and flavopurpurin behave similarly to (I). To Al alizarate the constitution (A) ($\text{R} = \text{H}$) is ascribed, its reaction with cold NaOH giving the salt (A; $\text{R} = \text{Na}$) from which it is regenerated by acidification. Boiling NaOH causes the production of (I) and of $\text{Al}(\text{ONa})_3$. Dyeing animal fibres with alizarin-red does not necessitate the presence of Ca although this is frequently advocated. It is possible to dispense with the use of Turkey-red oil and hence also with the steaming. H. W.



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Halochromy phenomena in perylene, its quinones and substitution products.—See A., 1938, I, 385.

Pyrogenesis of alkali menthoxides. M. BRAMBILLA (Annali Chim. Appl., 1938, 28, 209–217).—Heating to $300\text{--}550^\circ$ dehydrogenates Li, Na, and K menthoxides successively to the corresponding

menthone derivatives and thymoxides. The rate of decomp. of the menthoxides decreases with decrease in at. wt. of the metal, the reverse being true for their rate of formation from menthol and the metal.

F. O. H.

Synthesis of carane. P. C. GUHA and D. K. SANKARAN (Current Sci., 1938, 6, 606).—Et Δ^1 -tetrahydro-*p*-toluate with CMe_2N_2 at 0° for 2 weeks yields the *dicyclo*-(0:1:4)-heptane derivative,

$\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})\text{CMe}_2$, b.p. $150\text{--}160^\circ/6\text{ mm.}$, which on hydrolysis (5% alcoholic KOH) yields the corresponding carboxylic acid, m.p. $104\text{--}105^\circ$. Distillation (ZnO-BaO, reduced pressure) gives carane.

L. S. T.

Wagner-Meerwein rearrangement. Kinetic reinvestigation of the isomerisation of camphene hydrochloride. P. D. BARTLETT and I. PÖCKEL (J. Amer. Chem. Soc., 1938, 60, 1585—1590).—Rearrangement of camphene hydrochloride (I) to isobornyl chloride is catalysed by the HCl inevitably present as dissociation product of (I). Kinetic experiments in PhNO_2 and recognition of this dissociation lead to equations accounting quantitatively for previous results (cf. A., 1937, II, 288). The effect of HCl explains the slow rate of reaction in basic solvents (Et_2O , COMe_2). Cl^- is not a catalyst. *o*-Cresol is a strong and AcOH a weak catalyst.

R. S. C.

Salts of 3-bromo-*d*-camphor-10-sulphonic acid with organic bases. (SIGNA.) A. FEDERIGI and (SIGNA.) E. ORTENSII (Boll. Chim. farm., 1938, 77, 397—400).— $(\text{CH}_2)_6\text{N}_4$, m.p. $146\text{--}147^\circ$, $[\alpha]_D^{25} +57.75^\circ$ (all rotations in H_2O), *antipyrine*, m.p. $142\text{--}144^\circ$, $[\alpha]_D^{25} +54.27^\circ$, *pyramidone*, m.p. $150\text{--}152^\circ$, $[\alpha]_D^{25} +46.79^\circ$, and *piperazine 3-bromo-*d*-camphor-10-sulphonate*, m.p. 244° (decomp.), $[\alpha]_D^{25} +70.70^\circ$, are described.

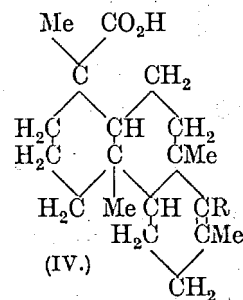
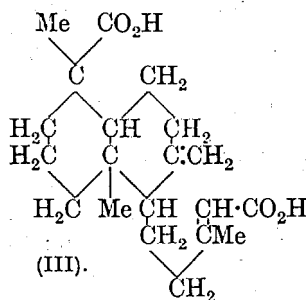
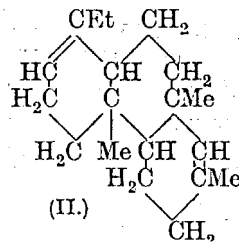
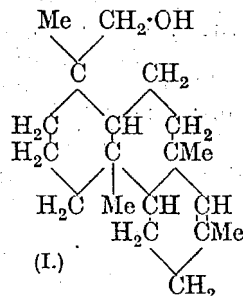
E. W. W.

Fenchene series. VIII. Reaction mechanism of the dehydration of fenchyl alcohol. G. KOMPPA and G. A. N. NYMAN (Annalen, 1938, 535, 252—266; cf. A., 1938, II, 149).—Dehydration of fenchyl alcohol is shown by the following and published reactions to yield primarily α -fenchene (I), methylsantene (II), and cyclofenchene; any β - (IV), γ - (V), or δ -fenchene formed arises by secondary rearrangement of (III). Use of $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ leads to (I) with some (III), (II), (IV), and (?) (V). (III) is converted only at $190\text{--}200^\circ$ by $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ into (IV), (V), and *iso*-fenchyl phthalate. Tschugaev's method gives (I) and (II) only. H_3PO_4 gives (III), (II), and (V) [(I) and (IV) are proved to be absent]; it converts (III) almost only into (II). KHSO_4 converts (III) into (V) and (IV). The products are identified mainly by oxidation.

R. S. C.

Diterpenes. XXXVII. Position of the carbonyl group in ring A of agathendiacid. L. RUZICKA and H. JACOBS (Rec. trav. chim., 1938, 57, 509—519; cf. A., 1938, II, 287).—Ag isonoragathate and MeI give difficultly separable *Me* esters, m.p. $109\text{--}110^\circ$, $[\alpha]_D^{25} +27.2^\circ$ in EtOH, and m.p. $92\text{--}93^\circ$, $[\alpha]_D^{25} -23.2^\circ$ in EtOH. The mixed esters are reduced by Na-MeOH, -EtOH, or $n\text{-C}_5\text{H}_{11}\cdot\text{OH}$ only with difficulty; in $n\text{-C}_5\text{H}_{11}\cdot\text{OH}$ mainly the amyl ester is

obtained. Rapid addition of a little EtOH to the mixed esters and Na in xylene at 120° gives, however, a fair yield of isonoragathenol (I), b.p. $160\text{--}161^\circ/0.1\text{ mm.}$, m.p. $120\text{--}121^\circ$; slow addition of the EtOH gives the *pinacol*, m.p. $222\text{--}226^\circ$. With $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ at $150\text{--}160^\circ$ (I) gives the *hydrocarbon* (II), b.p. $118\text{--}122^\circ/0.2\text{ mm.}$, dehydrogenated by Se at $330\text{--}340^\circ$ to 7-methyl-1-ethylphenanthrene. This proves the formulæ of (I), (II), agathendiacid (III), isagathendiacid [(IV); $\text{R} = \text{CO}_2\text{H}$], and isonoragathic



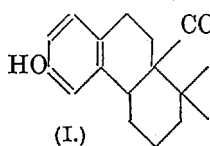
acid [(IV); $\text{R} = \text{H}$]. The position of the ethylenic linkings is open to doubt. By similar methods Et abietate gives 95% of abietinol, b.p. $163\text{--}167^\circ/0.1\text{ mm.}$, and thence readily a *hydrocarbon*, $\text{C}_{20}\text{H}_{30}$, b.p. $127\text{--}129^\circ/0.7\text{ mm.}$, and homoretene, new m.p. $81\text{--}82^\circ$. M.p. are corr.

R. S. C.

Recent progress in the chemistry of the terpenes. R. DULOU (Chim. et Ind., 1938, 40, 3—18).—A review.

Podocarpic acid. I. I. R. SHERWOOD and W. F. SHORT (J.C.S., 1938, 1006—1013).—Podocarpic acid, (I), $\text{C}_{17}\text{H}_{22}\text{O}_3$, m.p. 193° , $[\alpha]_{578}^{25} +144^\circ$, has been shown to be tricyclic and to contain a phenolic nucleus. (I) forms an Ac derivative, m.p. $173\text{--}176^\circ$ (cf. Oudemans, J. pr. Chem., 1874, 9, 385), and with $\text{Me}_2\text{SO}_4\text{-NaOH}$ gives Me podocarpate (II), m.p. 208° (lit. 174°) (Bz derivative, m.p. 143.5°); Et, m.p. 161° , and *p*-nitrobenzyl podocarpate, m.p. 204° , are similarly prepared. MeI-Na and (II) or (I) and $\text{Me}_2\text{SO}_4\text{-NaOH}$ -EtOH yield Me *O*-methylpodocarpate, m.p. 128° , hydrolysed with difficulty to *O*-methylpodocarpic acid, m.p. 158° . Distillation of (I) with Zn affords 1-methylphenanthrene (*styphmate*, m.p. $152\text{--}153^\circ$). Dehydrogenation (Se) of (I) gives this hydrocarbon and a phenol, $\text{C}_{15}\text{H}_{12}\text{O}$, m.p. 161° (*picrate*, m.p. 182° ; *acetate*, m.p. $118\text{--}119^\circ$; *benzoate*, m.p. 147° ; *glycollic ether*, m.p. 191°), the Me ether, m.p. $87\text{--}87.5^\circ$ (*picrate*, m.p. $140\text{--}141.5^\circ$), of which is oxidised to a quinone, m.p. 189° (*quinoxaline* derivative, m.p. 166°) [*acetoxy*, m.p. $182.5\text{--}183.5^\circ$, and *hydroxy-quinone*, m.p. 264--

265° (decomp.), by oxidation of the acetate]. The phenol is 6-hydroxy-1-methylphenanthrene and with NaOAc-NH₄Cl-AcOH gives the corresponding *NHAc*-compound, m.p. 197.5—198° (amine, m.p. 151°; *iodomethylphenanthrene*, m.p. 144.5—145°). Distillation of Ca podocarpate yields *p*-cresol and carpine. The annexed provisional formula for (I) is suggested.



The following are also described: 5-bromo-6-hydroxy-1-methylphenanthrene, m.p. 124° (Me ether, m.p. 129—130°); 5-amino-6-hydroxy-1-methylphenanthrene hydrochloride, m.p. 243—245° (decomp.); 1-methyl-5:6-phenanthraquinone, m.p. 176—177° (decomp.); 5:6-diacetoxy-1-methylphenanthrene, m.p. 154.5—155°. F. R. S.

Occurrence of ursolic acid in *Escallonia tortuosa*. Conversion of ursolic acid into α -amyrin. J. A. GOODSON (J.C.S., 1938, 999—1001).—Ursolic acid, protocatechuic acid, hydrocarbon, and fatty acid have been isolated. Monoacetylursolic acid and SOCl₂ give *acetylursoloyl chloride*, m.p. 224—226°, [α]_D²⁵ +53.3° in C₆H₆, reduced (Pd-H₂) to *acetylursol-aldehyde*, m.p. 244°, [α]_D²⁵ +71.4° in C₆H₆, of which the *semicarbazone*, m.p. 264—267°, [α]_D²⁵ +50.7° in EtOH, is converted by Na-EtOH into α -amyrin.

F. R. S.

Reaction of kojic acid with aldehydes. H. N. BARHAM and G. N. REED (J. Amer. Chem. Soc., 1938, 60, 1541—1545).—Kojic acid, the appropriate aldehyde, and a little NH₃ in hot EtOH give the 6:6'-methylene, m.p. 248.3° (*Ac*₄ derivative, m.p. 105—107°), -ethylidene, m.p. 211.2—212° (*Ac*₄ derivative, m.p. 134—136°), -n-propylidene, m.p. 217.5—218°, -n-butylidene, m.p. 192.4—193°, -n-amylidene, m.p. 185.6—187.2°, -n-hexylidene, m.p. 144—147°, -n-heptylidene, m.p. 152.6—153.6°, -benzylidene (I), m.p. 242.4° (decomp.) (*Ac*₄ derivative, m.p. 166—168°), - γ -phenylpropylidene, m.p. 182—183.5°, -cinnamylidene, m.p. 175—176°, -2-furfurylidene, m.p. 210—211°, and -allylidene, m.p. >250°, derivatives. CH₂O, but not other aldehydes, react similarly in H₂O. Resins are also formed during condensation in EtOH, and to a larger extent in H₂O, probably by further reaction similar to that involved in phenol-aldehyde resin formation. The structures ascribed to the products follow from analyses and from formation of unstable compounds with PhN₂Cl (PhN₂ attached to the phenolic OH). Kojic acid and PhN₂Cl give a stable product. (I) is also obtained [m.p. 250—256° (decomp.)] by CHPhCl₂ in PhNO₂ at 100—150°. M.p. are corr.

R. S. C.

Saponins and sapogenins. VI. Surface films of chlorogenin and [its] derivatives. C. R. NOLLER.

VII. Structure of the side-chain of chlorogenin. F. M. McMILLAN and C. R. NOLLER (J. Amer. Chem. Soc., 1938, 60, 1629—1630, 1630—1633; cf. A., 1937, II, 346).—VI. The surface films of chlorogenin (I) and its diacetate are highly compressible; that of the derived diketone collapses at about 6 dynes per cm. These facts confirm location of the 2 OH of (I) in different rings and the relationship of (I) and gitogenin.

VII. *Chlorogenin diacetate*, m.p. 154—155°, and

CrO₃ in AcOH at 32—33° (not 25° or 40°) give *chlorogenoic acid diacetate* (II), C₃₁H₄₆O₈, +H₂O, m.p. 114—116°, and anhyd., m.p. 210—211° (no semicarbazone; Me ester, m.p. 163°), hydrolysed to *chlorogenoic acid*, C₂₇H₄₂O₆, m.p. 169—170° (sinters at 161°). At, e.g., 40° a small amount of a *diacetoxy-lactone*, (?) C₂₆H₃₈O₆, + MeOH, or C₂₇H₄₄O₇, m.p. 249—252°, is obtained; hydrolysis gives the (OH)₂-lactone, C₂₂H₃₄O₄, + MeOH, or C₂₃H₄₀O₅, m.p. 255—256°. Further oxidation of (II), e.g., by KMnO₄, gives only a trace of an acid, C₂₇H₄₂O₆, m.p. 221—222°. With conc. HCl-AcOH (I) gives a very small amount of a ketone, yielding an impure semicarbazone, m.p. 114—118°. It is concluded that the side-chain of (I) resembles that of other steroid sapogenins.

R. S. C.

Constituents of pyrethrum flowers. XII. Nature of the side-chain of pyrethrolone. F. B. LAForge and H. L. HALLER (J. Org. Chem., 1938, 2, 546—559; cf. A., 1938, II, 239).—The following reactions indicate, although not conclusively, that the ethylenic linkings in the side-chain of pyrethrolone (I) are not conjugated. Al-Hg (prep. described) in Et₂O reduces the OH of (I), yielding *pyrethrene* (II), b.p. 85—87°/0.35 mm. [*semicarbazone*, m.p. 216—218° (decomp.); *oxime*, m.p. 67° (*Bz* derivative, m.p. 94°); *p*-nitrophenylhydrazone, m.p. 139°], reduced by H₂-PtO₂ in EtOH to the H₄-ketone (*dihydrojasmon*) (III) and by Zn dust in HBr-AcOH to *dihydro-pyrethrene*, b.p. 115—118°/11 mm. [*semicarbazone*, m.p. 202°, hydrogenated (PtO₂) in EtOH to the semicarbazone of (III)]. Br adds to (II), but loss of HBr is so rapid that the reaction appears as substitution. There is no sign of 1:4-addition. Adding 1 mol. of Br in AcOH or EtOH gives 1 mol. of HBr and reducing the product with Zn dust regenerates (II). 2 mols. of Br similarly give 2 mols. of HBr and an oily product, reduced by Zn to (II) and other substances. Adding 2 mols. of Br to (I) gives 2 HBr and a product which regenerates (I). 1:2-Napthaquinone does not react with (I) or (II), and (CH₃CO)₂O gives resins. (II) absorbs 2 O from BzO₂H, but the product is unstable, and the Br-derivative of (I) does not react. When (II) is oxidised with KMnO₄, only H₂C₂O₄ is obtained. O₃ and (I) in CCl₄ at 0° give 23% of MeCHO; tetrahydro-pyrethrolone gives MeCHO and (?) CH₂O; (II) gives 15% of MeCHO. Heating (II) with Na in Et₂O gives a Na compound, converted by CO₂ into an amorphous acid. Attempts to add 1 H₂ to (II) give only (III) and unchanged (II).

R. S. C.

Identification and constituents of the poisonous plants *huang-t'eng* and *tsai-chung-yao*. P. F. MEI and T. Q. CHOU (Chinese Med. J., 1938, 54, 37—39; cf. A., 1936, 1572).—The plants are probably identical with *Tripterygium Wilfordii*, Hook. They yield tripterin (changed to a compound, C₂₅H₃₄O₄, m.p. 219°, containing COMe₂ by recrystallisation from COMe₂; compound reconverted into tripterin by recrystallisation from Et₂O) and approx. 1.5% of dulcitol.

W. McC.

Onocerin. J. ZIMMERMANN (Helv. Chim. Acta, 1938, 21, 853—859).—Crude onocerin (I), isolated from the roots of *Ononis spinosa*, has m.p. (indef.) 205—226° whereas that derived by hydrolysis of the

diacetate (II), m.p. 224°, $[\alpha]_D +29.4^\circ$ in CHCl_3 , has m.p. 202–203°. Oxidation (CrO_3 in AcOH) of (I) affords onocerindiketone, m.p. 185° (*dioxime*, m.p. 236°). Similar oxidation of (II) yields the *diketone diacetate*, $\text{C}_{34}\text{H}_{48}\text{O}_6$, m.p. 302–303° (*dioxime*, m.p. 330°). Hydrogenation (Pt in warm AcOH) of (II) yields *tetrahydro-onocerin diacetate* (III), m.p. 218°, $[\alpha]_D +57.1^\circ$ in CHCl_3 , which does not give a colour with $\text{C}(\text{NO}_2)_4$; it is hydrolysed to *tetrahydro-onocerin*, m.p. 255°, oxidised to the corresponding *diketone*, m.p. 209–211° (*dioxime*, $\text{C}_{30}\text{H}_{50}\text{O}_2\text{N}_2$, m.p. 253–254°). The mother-liquors from (III) contain a substance hydrolysed to a *diol*, m.p. 187° (*diacetate*, m.p. 170°, $[\alpha]_D +55.2^\circ$ in CHCl_3), which is oxidised to a *diketone*, m.p. 154° (*dioxime*, $\text{C}_{30}\text{H}_{50}\text{O}_2\text{N}_2$, m.p. 248°). Crude (I) is converted by boiling 90% HCO_2H into the *diformate*, $\text{C}_{32}\text{H}_{46}\text{O}_4$, m.p. 226° (vac.), $[\alpha]_D +104^\circ$ in CHCl_3 , hydrolysed to a *diol* (IV), m.p. 230° (vac.) [corresponding *diacetate*, m.p. 260° (vac.), $[\alpha]_D +106^\circ$ in CHCl_3 , also obtained from (II) and HCO_2H]. (IV) is oxidised to a *diketone*, m.p. 170° (*oxime*, $\text{C}_{30}\text{H}_{46}\text{O}_2\text{N}_2$, m.p. 244°). It is therefore probable that (I) is not a pentacyclic triterpene, into which, however, it is converted by boiling HCO_2H . H. W.

Functional groups of adermin. R. KUHN and G. WENDT (Ber., 1938, 71, [B], 1534–1535).—Vitamin- B_6 hydrochloride is converted by CH_2N_2 in MeOH into *adermin Me ether*, m.p. 89.5–90°, which does not give a colour reaction with FeCl_3 or couple with $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2^+$. It is transformed by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ into *diacetyladermin Me ether* (I), m.p. 53–54°. All three O of adermin belong to OH, of which one is phenolic and the others are alcoholic. Active H cannot be detected in (I) at an increased temp. The N of the vitamin is ring-*tert*. H. W.

Rottlerin. IV. K. S. NARANG, J. N. RAY, and B. S. ROY (Current Sci., 1938, 6, 606–608).—A defence of the $\text{C}_{31}\text{H}_{30}\text{O}_8$ formula for rottlerin and a criticism of the views of Robertson *et al.* (A., 1938, II, 199). L. S. T.

Heparin. T. ASTRUP and H. B. JENSEN (J. Biol. Chem., 1938, 124, 309–312).—Crude heparin purified by repeated centrifuging in N-NaOH and N-NaOH-NaCl and treatment with AcOH and fuller's earth etc. gives with $\text{Ba}(\text{OAc})_2\text{-Ba}(\text{OH})_2$ a Ba salt which with Na_2SO_4 gives, after repeated pptn. by NaCl in COMe_2 and in EtOH , the Na salt, $\text{C}_{26}\text{H}_{36}\text{O}_{41}\text{N}_2\text{S}_4\text{Na}_8$ (vac.-dried) [corresponding with $\text{C}_{26}\text{H}_{78}\text{O}_{58}\text{N}_2\text{S}_4$ (air-dried heparin); cf. A., 1936, 1535], $[\alpha]_D^{24} +43.7^\circ$ (in H_2O ?). In boiling 0.1N-HCl, this is inactivated in 3 min.; from the product a Ba salt, $\text{C}_{38}\text{H}_{52}\text{O}_{52}\text{N}_2\text{S}_2\text{Ba}_3$, is obtained, corresponding with an inactivated heparin, $\text{C}_{19}\text{H}_{29}\text{O}_{26}\text{NS}$, in which 1 hexosamine and 3 SO_3H groups have been lost. As BaSO_4 equiv. to only 1 SO_3H is found, 2 SO_3H may be bound to the hexosamine. E. W. W.

Mechanism of the formation of γ -acetopropyl [8-keto-*n*-amyl] alcohol during hydrogenation-hydration of 2-methylfuran. Consecutivity of hydrogenation of the ethylenic linkings of 2-methylfuran. K. TOPTSCHIEV (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 497–498).—Hydrogenation-hydration of 2-methylfuran gives the 4:5-

H_2 -derivative, which hydrates to 2-hydroxy-2-methylfuran; by ring-fission this gives $\text{COMe}\cdot[\text{CH}_2]_3\cdot\text{OH}$, which is the only product isolated (Russ. Pat. 48,104, 1937). R. S. C.

Attempted partial asymmetric synthesis. D. DUVEEN (Compt. rend., 1938, 206, 1974–1976).— α -Furylmethylcarbinol (I), $[\alpha]_{461}^{15} -23.85^\circ$ (cf. A., 1936, 858), with H_2 (8 atm.)–Raney Ni at 70–80° affords α -tetrahydrofurylmethylcarbinol (II), $[\alpha]_{461}^{17} +8.86^\circ$, which cannot be converted into α -chloroethyltetrahydrofuran (III). The conversion of (I) into (II) introduces a second asymmetric C. Removal of the original centre of asymmetry, which involves the formation of (III), is impossible because (III) cannot be isolated. J. L. D.

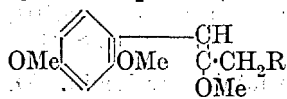
Aluminium chloride, a new reagent for the condensation of β -ketonic esters with phenols.

II. Condensation of 2:4-dihydroxy-5-ethylbenzoic acid and its methyl ester with ethyl acetoacetate. S. M. SETHNA and R. C. SHAH (J.C.S., 1938, 1066–1069; cf. A., 1938, II, 152).—Me 2:4-dihydroxy-5-ethylbenzoate and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ with AlCl_3 give *Me 5-hydroxy-4-methyl-8-ethylcoumarin-6-carboxylate*, m.p. 186–187° (Ac, m.p. 183–185°, and Bz derivatives, m.p. 154–156°; *Me ether*, m.p. 87–88°), hydrolysed to the acid, m.p. 242° (efferv.) (*Ph ester*, m.p. 134–135°). The ester with AcOH-HCl in a sealed tube affords *5-hydroxy-4-methyl-8-ethylcoumarin*, m.p. 212–213° (Ac, m.p. 112–114°, and Bz derivatives, m.p. 173–174°; *Me ether*, m.p. 107–109°), which with $\text{Me}_2\text{SO}_4\text{-NaOH}$ yields 2:6-dimethoxy- β -methyl-3-ethylcinnamic acid, m.p. 119–121°. The condensations may be effected in smaller yield with H_2SO_4 . F. R. S.

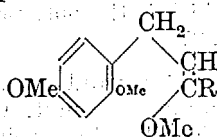
Natural coumarins. XXXVII. Skimmin. E. SPÄTH and O. NEUFELD (Rec. trav. chim., 1938, 60, 535–540; cf. A., 1938, II, 152).—Skimmin, $\text{C}_{15}\text{H}_{16}\text{O}_8$, $+\text{H}_2\text{O}$, m.p. 219–221° (decomp.), $[\alpha]_D^{18} -79.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (tetra-acetate, m.p. 183–184°, $[\alpha]_D^{18} -62.7^\circ$ in $\text{C}_5\text{H}_5\text{N}$), is proved to be umbelliferone β -glucoside by identification of the umbelliferone and glucose formed by hydrolysis, and by synthesis (m.p. 221–222°) from umbelliferone and acetobromoglucose. R. S. C.

Egonol. I. Constitution of egonol and a new permanganate oxidation process, "the benzene method." S. KAWAI and T. MIYOSHI (Ber., 1938, 71, [B], 1457–1464).—Extraction of the fruits of *Styrax japonicum*, Sieb. and Zucc., with Et_2O gives "egonoki" oil, hydrolysed by $\text{KOH-H}_2\text{O-EtOH}$ to egonol (I), $\text{C}_{20}\text{H}_{18}\text{O}_5$, m.p. 117.5–118°, b.p. 228–230°/0.15 mm., which contains 1 OMe, 1 OH [acetate, m.p. 107–107.5°, re-converted into (I) by hydrolysis; *p*-nitrophenylurethane, m.p. 208.5–209°], and CH_2O_2 (since it gives piperonylic acid when oxidised); the fifth O is in an ether bridge. (I) is optically inactive but evidence is adduced in favour of the view that this is due to racemisation during hydrolysis and that the natural material is optically active. (I) does not react with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ in C_6H_6 and is unaffected by Me_2SO_4 and alkali; OH is therefore *sec.* or *tert.* Very mild oxidation of (I) with CrO_3 in AcOH gives quantitatively only a polymeride of high m.p. KOH-

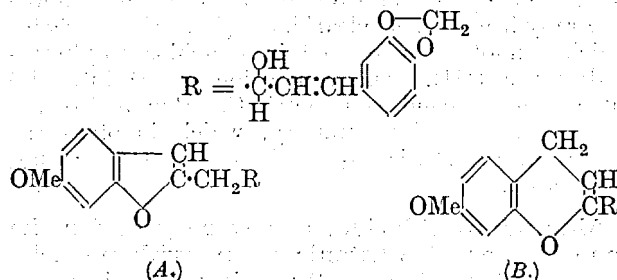
EtOH under pressure transforms (I) into *egonol hydrate* $\text{Me}_2\text{ ether}$ (IIa or IIb), m.p. 125–126°, which



(IIa.)



(IIb.)



(A.)

(B.)

does not condense with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$. For (I) the structure *A* or *B* is adduced.

Good results are obtained by oxidising with aq. KMnO_4 the well-agitated, emulsified C_6H_6 solution of (I) in H_2O . H. W.

Synthesis of α -tocopherol. P. KARRER, H. FRITZSCHE, B. H. RINGIER, and H. SALOMON (Helv. Chim. Acta, 1938, 21, 820–825).—Synthetic α -tocopherol (I), obtained from trimethylquinol (II) and phytol bromide, is converted by 3-bromocamphorsulphonyl chloride in $\text{C}_5\text{H}_5\text{N}$ into a *bromocamphorsulphonate*, m.p. 48–50°, $[\alpha]_D^{20} +29.93 \pm 2^\circ$, identical with that derived from natural (I). Allyl bromide, (II), and anhyd. ZnCl_2 in boiling light petroleum give 5-hydroxy-2:4:6:7-tetramethylcoumaran or 6-hydroxy-5:7:8-trimethylchroman, m.p. 126–127°. The *allophanate* of the product from geranyl bromide and (II) has m.p. 158°. Dimethylquinol reacts readily with $\alpha\beta$ -unsaturated alkyl halides, usually giving mixtures of compounds. Neotocopherol, allyl bromide, and ZnCl_2 give *allylneotocopherol* (*allophanate*, m.p. 165°). H. W.

Vitamin-E. Synthesis of α -tocopherol. F. BERGEL, A. JACOB, A. R. TODD, and T. S. WORK (Nature, 1938, 142, 36).—Racemic α -tocopherol has been synthesised by heating phytol and ψ -cumoquinol in presence of ZnCl_2 (cf. A., 1938, II, 290). 6-Hydroxychromans, 5-hydroxycoumarans, and α - and β -tocopherol are almost identical as regards absorption spectrum, reducing properties, and the effect of esterification on the absorption spectrum. Recent degradation evidence favours a chroman structure for the tocopherols. L. S. T.

Vitamin-E. I. Structure and synthesis of α -tocopherol. L. I. SMITH, H. E. UNGNADE, and W. W. PRICHARD (Science, 1938, 88, 37–38).— α -Tocopherol (I) has been synthesised from trimethylquinol (II) and phytol bromide without the aid of a catalyst, and from (II) and phytadiene. 6-Hydroxypentamethylchroman has been synthesised (a) from (II) and $\gamma\gamma$ -dimethylallyl bromide, (b) from (II) and isoprene, and (c) from 6-hydroxy-5:7:8-trimethyl-3:4-dihydrocoumarin and MgMeI . These syntheses indicate that Fernholz's structure for (I) (A., 1938, II, 186) is correct (cf. *ibid.*, 290). L. S. T.

Vitamin-E. III. Permanganate oxidation of α -tocopherol. O. H. EMERSON (Science, 1938, 88, 40).—Oxidation of α -tocopherol (I) in COMe_2 with neutral KMnO_4 affords a good yield of the $\text{C}_{21}\text{H}_{40}\text{O}_2$ lactone which was isolated as the benzylthiuronium salt of its OH-acid. Admixture with the corresponding salt obtained by the CrO_3 oxidation of (I) produced no depression of the m.p. Further support for the chroman structure of (I) is thus afforded. L. S. T.

Vitamin-E.—See A., 1938, III, 680.

Unsaponifiable matter of wheat germ oil. β -Tocopherol. A. ICHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 627–628; cf. A., 1938, III, 358).— β -Tocopherol *allophanate* has $[\alpha]_D +6.37^\circ$ in CHCl_3 . Pyrolysis gives a sublimate, m.p. 165°. α -Tocopherol *allophanate* has not been obtained, possibly owing to change during working up. R. S. C.

Flavones from the dibromides of *o*-hydroxyphenyl styryl ketones. Modified synthesis of apigenin and luteolin. W. A. HUTCHINS and T. S. WHEELER (Current Sci., 1938, 6, 605).—The dibromides of certain *o*-hydroxyphenyl styryl ketones give better yields of the flavones by treatment with KCN-EtOH (cf. A., 1938, II, 18). *o*-Hydroxyphenyl α -bromo- β -ethoxy- β -alkoxyphenylethyl ketones give flavones with KCN-EtOH . 2-Hydroxy-4:6-dimethoxyphenyl *p*-methoxystyryl ketone is brominated to 5-bromo-2-hydroxy-4:6-dimethoxyphenyl $\alpha\beta$ -dibromo- β -*p*-anisylethyl ketone which, when heated, gives 6-bromo-5:7:4'-trimethoxyflavone; with HI this gives apigenin. Luteolin is synthesised by heating 5-bromo-2-hydroxy-4:6-dimethoxyphenyl $\alpha\beta$ -dibromo- β -3:4-dimethoxyphenylethyl ketone with KCN-EtOH and treating the *bromoflavone* formed with HI. L. S. T.

Nobiletin. I. K. F. TSENG. II. R. ROBINSON and K. F. TSENG (J.C.S., 1938, 1003–1004, 1004–1006).—I. An oil extracted by cold MeOH from *Citrus nobilis*, Lour, affords *nobiletin* (I), $\text{C}_{15}\text{H}_{14}\text{O}_2(\text{OMe})_6$, m.p. 134°, hydrolysed (EtOH-KOH) to veratric acid.

II. Hydrolysis of (I) with EtOH-KOH yields acetoveratrone, isolated as the oxime, and demethylation (HI) gives 5:6:7:8:3':4'-hexahydroxyflavone, m.p. 310–314° (decomp.) (Ac_6 , m.p. 226–228°, and Bz_6 derivatives, m.p. 235–236°), which is methylated (CH_2N_2) to 5-hydroxy-6:7:8:3':4'-pentamethoxyflavone, m.p. 145°. (I) is probably 5:6:7:8:3':4'-hexamethoxyflavone. F. R. S.

Colouring matter of red cabbage. III. I. CHMIELEWSKA, I. SMARDZEWSKA, and J. KULESZA (Rocz. Chem., 1938, 18, 176–184).—Rubrobrassin chloride (I) (A., 1937, II, 71) is hydrolysed by HCl in MeOH to cyanidin chloride and glucose, leaving a OMe originally present unaccounted for. Similar treatment of 3:3'- and 5:7-dimethylcyanidin does not result in elimination of Me, whence it is supposed that the aglucone of (I) does not contain OMe, but that the disaccharide removed by hydrolysis consists of glucose and an unknown methylxose. Carbo-methoxyvanillyl chloride and Et sodio- $\alpha\gamma$ -dimethoxy-acetoacetate interact in Et_2O , the solvent is distilled off, and the residue is boiled with 2.5% KOH for 2.5

hr., to yield 4-hydroxy-3-methoxyphenyl methoxymethyl ketone (II), b.p. 180°/22 mm., m.p. 62—63°. 3 : 4-Dihydroxyphenyl methoxymethyl ketone, m.p. 118° (decomp.), is prepared analogously from dicarbomethoxyprotocatechuy chloride. The product of acetylation of (II) condensed with 4 : 6-dihydroxy-2-benzoyloxybenzaldehyde in EtOH-EtOAc, by saturating with HCl at 0°, yields 5-benzoyl-3 : 3'-dimethylcyanidin chloride. This is hydrolysed with 2N-NaOH to 3 : 3'-dimethylcyanidin (chloride, +H₂O), which is not attacked by boiling HCl-MeOH. 6-Hydroxy-2 : 4-dimethoxybenzaldehyde and 3 : 4-diacetoxyphenyl acetoxymethyl ketone in anhyd. HCO₂H when treated with HCl at 0° yield 5 : 7-dimethylcyanidin chloride.

R. T.

New natural colouring matter of the naphthalene group. J. R. PRICE and R. ROBINSON (Nature, 1938, 142, 147—148).—Dunnione (I), C₁₅H₁₄O₃, orange-red needles from H₂O or light petroleum, m.p. 98—99°, occurs as a deposit on the leaves and inflorescences of *Streptocarpus Dunnii*, Mast. (I) is a β-naphthaquinone derivative, and its behaviour towards alkalis indicates that the O is a member of an easily-ruptured chroman or coumaran ring. Acidification of the alkaline solution obtained under certain conditions does not regenerate (I), but forms a new substance which is probably an α-naphthaquinone derivative. The formation of MeCHO by oxidation with alkaline H₂O₂ and the 1.6 mols. of AcOH produced on oxidation with CrO₃ indicate that (I) is 2 : 3 : 3-trimethyl-6 : 7-benzocoumaran-4 : 5-quinone or the isomeride with the CMe₂ directly attached to O.

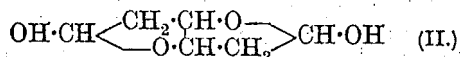
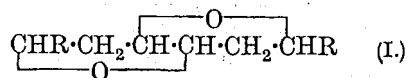
L. S. T.

Derivatives of 1 : 4-dioxan. VII. F. P. A. TELLEGEN [with, in part, C. VERMANDE, C. KUYLAAS, J. EHRENBURG, P. MALTHA, and J. VAN DALEN] (Rec. trav. chim., 1938, 57, 667—672; cf. A., 1938, II, 110).—2 : 3-Dichlorodioxan with CH₂Br·CH₂·OH (I) or CHPh₂·CH₂·OH (II) in hot C₆H₆ gives 2 : 3-di-β-bromo- (III), m.p. 41—43°, and 2 : 3-di-β-β-diphenyl-ethylidioxan, m.p. 121.5—122.5°, the rate of reaction being (II) < (I) < CH₂Cl·CH₂·OH. In boiling PhMe, PhOH (or NaOPh in COMe₂) and p-NO₂·C₆H₄·OH give 2 : 3-diphenoxy-, m.p. 119—121°, and 2 : 3-di-p-nitrophenoxy-dioxan, m.p. 220—222° (reduced by SnCl₂ or Na₂S to p-NH₂·C₆H₄·OH), respectively. NaI in COMe₂ converts (III) into 2 : 3-di-β-iodoethoxydioxan, m.p. 51—52°. (II) is obtained from CHPh₂·OMe by successive action of Na and (CH₂O)₃. CHPh₂·CHO is unaffected by Al(OEt)₃ or H₂-Pd-C, and with H₂-Pt gives only a little CHPh₂·OH. The halogeno-ethers do not react with Mg. Heating CHCl₂·CH(OEt)₂ with (CH₂·OH)₂ and H₂SO₄ with removal of the Et₂O formed gives 54% of 2-dichloromethyl-1 : 3-dioxacyclopentane, b.p. 188—191°/760 mm., 94°/20 mm. (cf. Meldrum *et al.*, A., 1936, 708), converted by Bz₂O-H₂SO₄ into CHCl₂·CHO and (CH₂·OBz)₂.

R. S. C.

Sesamin. II. W. D. COHEN (Rec. trav. chim., 1938, 57, 653—658; cf. A., 1929, 298).—Sesamin and Br-AcOH give the Br₂-derivative [(I); R = 2 : 5 : 6-C₆H₂Br₂O₂CH₂], m.p. 180.5—181°, [α]_D -9.6° in CHCl₃, converted by HNO₃ into 1 : 2 : 5 : 4-CH₂O₂·C₆H₂Br·NO₂ and an oily substance (?) (II).

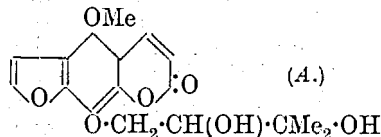
The structure of (II) is based on the reduction of AgNO₃-NH₃ only when hot or in presence of KOH,



on the very slow reaction with fuchsin-SO₂, on the inertness towards Fehling's solution, and on formation in dil. HCl of (? βγ-)dihydroxyadipdialdehydedi-2 : 4-dinitrophenylhydrazone.

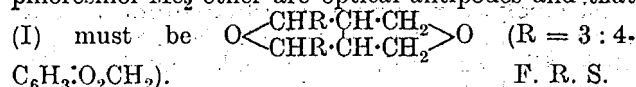
R. S. C.

Chemical constituents of Umbelliferæ. VI. Constituents of the root of *Angelica glabra*, Makino. T. NOGUCHI and M. KAWANAMI (Ber., 1938, 71, [B], 1428—1430).—Aminobergaptin is converted by diazotisation into 8-hydroxy-5-methoxypsoralen, m.p. 212° (decomp.), identical with the phenol obtained by the action of AcOH-H₂SO₄ on Byak-angelicin (I). The Et ether of this phenol is identical with 5-methoxy-8-ethoxypsoralen, m.p. 140—141°. (I) is therefore A.



H. W.

Synthesis of eudesmin and pinosresinol dimethyl ether from l-asarinin and d-sesamin. T. KAKU and H. RI (Keijo J. Med., 1938, 9, 5—20).—l-Asarinin (I) or d-sesamin with KOH-MeOH, followed by CH₂N₂, may be converted into epieudesmin, m.p. 133—134°, [α]_D²⁰ -144.8° in CHCl₃ (normal form), eudesmin, m.p. 107—108°, [α]_D²⁰ -64.2° in CHCl₃, or epipinosresinol Me₂ ether, m.p. 133—134°, [α]_D²⁰ +145.5° in CHCl₃ (normal form, pinosresinol Me₂ ether, m.p. 107—108° [α]_D²⁰ +64.3° in CHCl₃). The following derivatives are described: r-epieudesmin, m.p. 121—122°; dinitroepieudesmin, m.p. 159—161°, [α]_D²⁷ -73.9° in CHCl₃, and m.p. 222—225°; dinitro-eudesmin, m.p. 212°, [α]_D²⁷ +125.5° in CHCl₃; mononitro-eudesmin, m.p. 168—170°, [α]_D²⁷ +141.8° in CHCl₃; dinitroepipinosresinol Me₂ ether, m.p. 159—161°, [α]_D²⁷ +73.7° in CHCl₃; r-dinitroepieudesmin, m.p. 219—220°; dinitropinosresinol Me₂ ether, m.p. 212—213°, [α]_D²⁴ -124.6° in CHCl₃; mononitropinosresinol Me₂ ether, m.p. 169—171°, [α]_D²⁷ -143.2° in CHCl₃; r-dinitro-eudesmin, m.p. 240—241°; dibromoepieudesmin, m.p. 160—161°, [α]_D²⁷ -106.3° in CHCl₃; dibromoeudesmin, m.p. 173° [α]_D²⁷ +69.3°; dibromoepipinosresinol Me₂ ether, m.p. 160—161°, [α]_D²⁷ +107.1° in CHCl₃; dibromopinosresinol Me₂ ether, m.p. 173°, [α]_D²⁷ -68.5° in CHCl₃; r-dibromoeudesmin, m.p. 157—158°, and r-dibromoeudesmin, m.p. 177—178°. The conclusion is reached that eudesmin and pinosresinol Me₂ ether are optical antipodes and that (I) must be



F. R. S.

Acid properties of pyrrole. M. DEŽELIĆ and B. BELIA (Annalen, 1928, 535, 291—300).—Measurements of η indicate by max. the existence of 2 : 1, 1 : 1,

or 1 : 2 compounds of pyrrole with $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ (I), β -picoline, and quinoline, of 2 : 4-dimethylpyrrole with (I), piperidine (II), and nicotine (III), and of 2 : 4-dimethyl-3-ethylpyrrole with (II) and (III). Evolution of heat on mixing indicates reaction of pyrrole with NEt_3 . Acids, EtOH, and PrCHO do not form compounds. The acidity of pyrrole thus proved is connected with the aromatic nature of the ring, for which an electronic structure is given. R. S. C.

Heterocyclic ketones. II. β -Amino-ketones containing thiophen, thiazole, and furan nuclei, and their behaviour towards phenylhydrazine. G. A. LEVY and H. B. NISBET (J.C.S., 1938, 1053—1056).—The syntheses of β -amino-ketones of the type $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NR}_2\cdot\text{HCl}$ from 2-acetylthiophen, 2-acetyl-4-phenylthiazole, and 2-acetylfuran by the Mannich reaction are described: 2-thienyl β -piperidinomethyl, m.p. 199°, and β -dimethylaminomethyl ketone hydrochloride, m.p. 172°; 4-phenyl-2-thiazolyl β -piperidinoethyl, m.p. 193—195° (decomp.), β -dimethylaminomethyl, m.p. 174°, β -diethylaminomethyl, m.p. 142°, and β -di-n-propylaminomethyl ketone hydrochloride; 2-furyl β -piperidinoethyl, m.p. 185—186°, β -di-n-propylaminomethyl, decomp. 129—130°, β -di-n-butylaminomethyl, m.p. 111°, and β -di-(β -hydroxyethyl)-aminomethyl ketone hydrochloride, m.p. 100—101°; 1-phenyl-3-(4'-phenyl-2'-thiazolyl)pyrazoline, m.p. 198°, obtained from $\text{NHPh}\cdot\text{NH}_2$ and any one of the 4-phenyl-2-thiazolyl compounds; and the phenylhydrazones of 2-acetyl-4-phenylthiazole, m.p. 141° (N-Ac derivative, m.p. 209°). F. R. S.

Pyridine and quinoline series. I. Historical. II. Synthesis of 4-hydroxymethylpiperidine from citric acid. III. Theory of the hydrogenation of nuclear carboxylic acids of the pyridine series to carbinols. P. RABE [with, in part, O. SPRECKELSEN, L. WILHELM, and H. HÜTER] (J. pr. Chem., 1938, [ii], 151, 65—81).—I. The relationship of $\text{C}_5\text{H}_5\text{N}$ and quinoline to the cinchona alkaloids is discussed.

II. 2 : 6-Dichloropyridine-4-carboxylic acid (I) is reduced (Sn and 30% HCl) to 2 : 6-dichloro-4-hydroxymethylpyridine, m.p. 133° (benzoate, m.p. 121°), which is converted (H_2 -Pd sponge in KOH-MeOH containing BaCO_3 at room temp.) into 4-hydroxymethylpyridine, m.p. (indef.) 47—50° [hydrochloride, m.p. 175° (decomp.); non-cryst. benzoate and its picrate, m.p. 186°], whence (H_2 -Pt sponge-1% H_2SO_4) the very hygroscopic 4-hydroxymethylpyridine, b.p. 118—120°/10 mm., m.p. 56—62°.

III. Treatment of pyridine-3- or -4-carboxylic acid with Sn and 30% HCl gives the corresponding carbinol in comparatively poor yield. Electrolysis of (I) at a Pb cathode in aq. or alcoholic H_2SO_4 or treatment of it with H_2 (Pd sponge in 10% H_2SO_4 or AcOH) does not cause replacement of halogen. This is effected by H_2 (Pd) in a basic medium. H. W.

Electrolytic reduction of glutarimide and its derivatives. B. SAKURAI (Bull. Chem. Soc. Japan, 1938, 13, 482—488).—Glutarimide and its N-Me, N-Et, and N-Ph derivatives are electrolytically reduced at a Pb cathode, best in 20—30, 50, 50, and 80—90% H_2SO_4 , respectively, to the piperidones in good yield. Further reduction in 50% H_2SO_4 at

a special Pb or Zn-Hg cathode gives the piperidine derivatives. N-Ethyl-, b.p. 250—260°, and N-phenylglutarimide, m.p. 145°, piperidone platinichloride, m.p. 176° (decomp.), N-ethyl-, b.p. 105—106° [platinichloride, m.p. 164° (decomp.)], and N-phenylpiperidone, m.p. 98° [platinichloride, m.p. 176° (decomp.)], N-ethyl- [platinichloride, m.p. 202° (decomp.)] and N-phenylpiperidine (platinichloride, +2 H_2O) are described. R. S. C.

Tautomerism of homologues of pyridine. Syntheses in the pyridine series. V. Condensation reactions. A. E. TSCHITSCHIBABIN (Rec. trav. chim., 1938, 57, 582—585; cf. A., 1938, II, 245).—Na derivatives of α - (I) and γ -picoline (II) and quinaldine (III) react with RHal as do Grignard reagents. Thus, addition of COPh_2 in (III) to NaNH_2 in (III) gives 2- α -hydroxy- α -diphenylethylquinoline, m.p. 160—162° (hydrochloride). (I) gives similarly a good yield of 2- α -hydroxy- α -diphenylethylpyridine, m.p. 142° (hydrochloride). Aliphatic ketones, however, give mainly condensation products derived from the ketone, and camphor gives also a very poor yield of tert. alcohol. PhCHO gives a little 2- α -hydroxy- α -phenylethylpyridine, the main products being those of the Cannizzaro reaction. MeOBz and EtOBz with (I) and NaNH_2 give mainly BzOH and NH_2Bz with some 2-phenacylpyridine (IV), m.p. 56°. PhCN , (I), and NaNH_2 give cyaphenin and the imine [hydrolysed to (IV)], but (II) gives only 4-phenacylpyridine, m.p. 100—105°. R. S. C.

Formation of 3 : 5-di-iodo-2(4)-hydroxypyridine from 2-halogenopyridines. Z. RODEWALD (Rocz. Chem., 1938, 18, 96—102).—2-Bromo- or 2 : 6-dibromo-pyridine heated at 185° (20 hr.) with conc. HI yields a mixture of 3 : 5-di-iodo-2- (I) and -4-hydroxypyridine (II). The process is represented : $\text{C}_5\text{H}_5\text{NBr}$ or $\text{C}_5\text{H}_3\text{NBr}_2 + \text{HI} \rightarrow \text{C}_5\text{H}_5\text{N} \rightarrow (+\text{I})$ 3 : 5-di-iodopyridine \rightarrow 3 : 4 : 5- and 2 : 3 : 5-tri-iodopyridine \rightarrow (+ H_2O) (I) and (II). Since $\text{C}_5\text{H}_5\text{N}$ and HI under similar conditions give only NH_3 and C_5H_{12} , it is supposed that the iodination of $\text{C}_5\text{H}_5\text{N}$ is catalysed by some unknown intermediate product. R. T.

Influences of alkyl groups in carbonyl compounds. E. E. AYLING (J.C.S., 1938, 1014—1023).—The effect of the nature of R in COR is that expected from electronic considerations when R takes part in the reaction. For k of RCO_2H , the m -nitration of ROBz , the prototropy of COPhR , and the Hantzsch reaction with aliphatic aldehydes (new, comparable data are provided) anomalies occur when $\text{R} = \text{Pr}^a$, becoming less marked with higher members; this is due to the terminal Me in COPr^a approaching closest to the CO and thus exerting the max. field effect (attraction of the unshared electrons of the O by Me). The following new data are recorded : b.p. of RCHO , $\text{R} = \text{Pr}^a$ 75.5°/755.5 mm., Bu^a 103°/767 mm., Bu^b 93°/764 mm., $\text{CHPh}\cdot\text{CH}$ 134°/19 mm., $\text{CH}_2\text{Ph}\cdot\text{CH}$ 101.5°/10.5 mm., and CH_2Ph 82°/10 mm.; Et_2 2 : 6-dimethyl-4-n-butyl- (I), m.p. 97°, -4- β -phenylethyl- (II), m.p. 112°, -4-n-propyl-, m.p. 125.5°, -4-isobutyl-, m.p. 97°, -4-n-amyl-, m.p. 56°, and -4-benzyl- (III), m.p. 119°, and 2 : 4 : 6-trimethyl-, m.p. 130°, -1 : 4-dihydropyridine-3 : 5-dicarboxylate. (III) or the corre-

sponding Pr^{β} ester (IV) with hot N-HNO_3 gives Et_2 2:6-dimethylpyridine-3:5-dicarboxylate, but (I) and (II) give Et_2 2:6-dimethyl-4-n-butyl-, b.p. 198—199°/16 mm., and 4- β -phenylethyl-pyridine-3:5-dicarboxylate (V), m.p. 34°, b.p. 246—247°/18 mm. (nitrate, m.p. 128°), respectively. With S at 170° or 200° (II), (III), and (IV) give Et_2 2:6-dimethyl-4-isopropyl-, b.p. 183°/11 mm., and 4-benzyl-pyridine-3:5-dicarboxylate, b.p. 225°/12 mm., m.p. 46° (hydrochloride, m.p. 89°), and (V). R. S. C.

Pyridine derivatives.—See B., 1938, 902.

Syntheses of pyrrole and indole derivatives by use of magnesiyl derivatives. Q. MINGOIA (Boll. Chim. farm., 1938, 77, 337—358).—A review.

E. W. W.

Preparation of isatin- β -oxime. V. HOVORKA and V. ŠÝKORA (Chem. Listy, 1938, 32, 241—243).—The β -oxime is prepared from isatin and $\text{NH}_2\text{OH}\cdot\text{HCl}$ in boiling aq. solution. R. T.

Synthesis of 6:7-dimethoxyquinoline. S. SUGASAWA, K. KAKEMI, and T. TSUDA (Proc. Imp. Acad. Tokyo, 1938, 14, 67—68).—2-Keto-6:7-dimethoxy-1:2:3:4-tetrahydroquinoline with P_2S_5 and K_2S in xylene yields 2-thion-6:7-dimethoxy-1:2:3:4-tetrahydroquinoline, m.p. 151°, which is reduced at a Pb cathode in $\text{EtOH-H}_2\text{SO}_4$ to 6:7-dimethoxy-1:2:3:4-tetrahydroquinoline, an oil (hydrochloride, m.p. 196°; NO_2 -, m.p. 137°, and *Bz* derivative, m.p. 102°), oxidised by Pd and cinnamic acid to 6:7-dimethoxyquinoline, an oil [hydrochloride, m.p. 232° (decomp.); picrate, m.p. 251—252° (decomp.)]. J. D. R.

Reaction between hydrazine hydrate and 4-chloroquinoline derivatives. O. G. BACKEBERG and C. A. FRIEDMANN (J.C.S., 1938, 972—977).—The compound, obtained by Koenigs *et al.* (A., 1935, 989) by heating N_2H_4 and 4-chloroquinoline at 150° in a sealed tube is 3:4-diaminoquinoline (I), m.p. 122° (platinichloride, decomp. >300°), the Ac_2 derivative, m.p. 193°, being converted by EtOH-HCl into 2:2'-dimethylquin(3:4:5':4')iminazole, m.p. 100° (picrate, m.p. 200°; platinichloride, decomp. >300°). HCO_2H and (I) yield 2-methylquin(3:4:5':4')iminazole, m.p. 97° (picrate, m.p. 210°). (I) is also obtained by the method of Marckwald and Chain (A., 1900, i, 521). 4-Chloro-6-, -5 (or -7)-, and -8-methyl-, -5:7-, and -6:8-dimethyl-quinoline all react similarly with N_2H_4 in a sealed tube. The following are described: 4-hydrazino-8-methyl-, m.p. 199°; 3:4-diamino-8-, m.p. 122° (picrate, m.p. 202°), and -6-methyl-, m.p. 153° [picrate, m.p. 208° (decomp.)]; 4-hydroxy-5(or 7)-methyl-, m.p. 273°; 4-chloro-5(or 7)-methyl-, m.p. 78° (picrate, m.p. 193°); 3:4-diamino-5(or 7)-methyl-, m.p. 150° [picrate, m.p. 212° (decomp.)]; 3:4-diamino-6:8-dimethyl-, m.p. 140° (picrate, m.p. 183°); 4-hydroxy-5:7-dimethyl-, m.p. 288° (decomp.) (picrate, m.p. 207°); 4-chloro-5:7-dimethyl-, m.p. 73° (picrate, m.p. 226°), and 3:4-diamino-5:7-dimethyl-quinoline, m.p. 150° (picrate, m.p. 214°), and 3:4-diaminoquinoline, m.p. 129° (picrate, m.p. 197°), and 4-anilino-3-methyl-quinoline, m.p. 219°. 4:4'-Azo-5:7:5':7'-tetramethylquinoline, m.p. 250° (decomp.), is also obtained

from N_2H_4 and 4-chloro-5:7-dimethylquinoline, 3:4-Dichloroquinoline, m.p. 67° (4-OH-compound, m.p. 340°), could not be converted into the corresponding $(\text{NH}_2)_2$ -compound, and nitration of 4-aminoquinoline gives 4-nitroaminonitroquinoline, decomp. 200°, and dinitro-4-aminoquinoline, m.p. 276°, reduced (Na_2S) to 4-aminonitroaminoquinoline, m.p. 220° (decomp.). F. R. S.

Reaction between phenylhydrazine and 4-chloroquinoline derivatives, and the preparation of the corresponding 4-benzeneazo- and 4-amino-compounds. O. G. BACKEBERG (J.C.S., 1938, 1083—1087).— $\text{NHPh}\cdot\text{NH}_2$ and 4-chloroquinolines react to form (i) the corresponding 4-phenylhydrazino-compound, if the reaction is carried out at 200° in an inert solvent, and (ii) the corresponding 4-amino-3-anilino-compound, if the reaction is in a sealed tube at 200°. The 4-phenylhydrazino-compounds are unstable in air, and are readily oxidised (FeCl_3) to the 4-benzeneazo-compounds, which can be reduced (Zn-HCl) to the 4- NH_2 -derivatives. The following are described: 4-phenylhydrazino-, m.p. 188° [hydrochloride, m.p. 284° (decomp.)], and 4-benzeneazo-quinoline, m.p. 100°; 4-amino-3-anilino-, m.p. 142° [hydrochloride, m.p. 218° (decomp.)], not identical with 4-p-aminoanilino-quinoline, m.p. 173°; 1'-phenyl-2:2'-dimethylquin(3:4:5':4')iminazole, m.p. 124° (platinichloride, decomp. >300°); 4-acetamido-3-anilinoquinoline, m.p. 117°; 4-phenylhydrazino-, m.p. 205°, 4-benzeneazo-, m.p. 104°, and 128°, 4-amino-, m.p. 205°, and 4-amino-3-anilino-, m.p. 100°, -6-methylquinoline; 4-benzeneazo-, m.p. 76°, 4-amino-, m.p. 161°, and 4-amino-3-anilino-, m.p. 137°, 5(or 7)-methylquinoline; 4-benzeneazo-, m.p. 104°, 4-amino-, m.p. 141°, and 4-amino-3-anilino-, m.p. 101°, -8-methylquinoline; 4-benzeneazo-, m.p. 126°, 4-amino-, m.p. 166°, and 4-amino-3-anilino-, m.p. 127°, -5:7-dimethylquinoline; 4-benzeneazo-, m.p. 117°, 4-amino-, m.p. 165°, and 4-amino-3-anilino-, m.p. 105°, -6:8-dimethylquinoline; 4-benzeneazo-, m.p. 105—109°, and 4-amino-6-ethoxyquinoline, m.p. 197°; 4-benzeneazo-, m.p. 117°, and 4-amino-8-ethoxyquinoline, m.p. 222°; 4-benzeneazoquinoline, m.p. 70° and 89°; 4-amino-3-anilinoquinoline, m.p. 134°; and 4-benzeneazo-, m.p. 133°, and 4-amino-3-methylquinoline, m.p. 189°. F. R. S.

Synthesis of 2:4-diarylaminoquinoline derivatives. II. K. DZIEWOŃSKI and W. DYMEX [with M. GŁOWACKA, M. KITLIŃSKI, and J. KUŹMA] (Rocz. Chem., 1938, 18, 145—157).—Di-*p*-tolylacetamidine and PhNCS at 220° (4 hr.) yield 4-anilino-2-*p*-toluidino-6-methylquinoline, m.p. 79° [hydrochloride, m.p. 274°; nitrate, m.p. 231°; picrate, m.p. 253°; NO -derivative, m.p. 153° (decomp.)], hydrolysed by NaOH-EtOH to 2-*p*-toluidino-4-hydroxy-6-methylquinoline, m.p. 300—305°, and this further to 2:4-dihydroxy-6-methylquinoline, m.p. >350°. NHPhAc and CO(NHPh)_2 (I) heated at 260° for 5 hr. yield 2:4-dianilinoquinoline [nitrate, m.p. 212° (decomp.)]; sulphate, m.p. 312°; NO_2 -derivative, m.p. 213—215°; Br-derivative (II), m.p. 194—196° (hydrobromide, m.p. 282°)]. 2-Anilino-4-hydroxyquinoline (III), PCl_5 , and POCl_3 (3 hr. at the b.p.) afford 4-chloro-2-anilinoquinoline, m.p. 161°. (III) in 15% KOH and Me_2SO_4 (30 min.

at the b.p.) yield 2-anilino-4-methoxyquinoline, m.p. 118—120°. (II) is hydrolysed by EtOH-NaOH (6 hr. at 220°) to 2(4)-anilino-dihydroxyquinoline, m.p. 318—320°. EtCO-NHPh, NH₂Ph, and (I) (3 hr. at 290°) yield 2:4-dianilino-3-methylquinoline, m.p. 190° [hydrochloride, m.p. 282—283°; picrate, m.p. 243° (decomp.); 2(4)-NO-derivative, m.p. 110° (decomp.); 2(4)-N-Ac derivative, m.p. 177°], from which a mixture of 4-anilino-2-, m.p. 260—262°, and 2-anilino-4-hydroxy-3-methylquinoline, m.p. 264—266°, is obtained by hydrolysis with EtOH-NaOH (220°; 8 hr.). CH₂Ph·CO-NHPh and (I) (280°; 3 hr.) afford 2:4-dianilino-3-phenylquinoline, m.p. 180—181° (picrate, m.p. 230—231°), hydrolysed as above to 4-anilino-2-, m.p. 295°, and 2-anilino-4-hydroxy-3-phenylquinoline, m.p. 236—238°, and by prolonged hydrolysis to 2:4-dihydroxy-3-phenylquinoline, m.p. 320—323°. *s*-Di-*p*-tolylcarbamide and NHPhAc (280°; 3 hr.) yield 2-anilino-4-*p*-toluidino-6-methylquinoline, m.p. 90—100° (hydrochloride, m.p. 250°). R. T.

Derivatives of 2-phenylquinoline-4-carboxylic acid. A. LESPAGNOL and (MLLE.) BAR (Bull. Sci. Pharmacol., 1938, 45, 200—203).—2-Phenylquinoline-4-carboxyl chloride hydrochloride, m.p. 135°, is obtained cryst. by the action of boiling SOCl₂ on the acid and separation from the cold liquid. Interaction of it in C₅H₅N with 2:1:3-OH·C₆H₃Me·CO₂H gives 2-phenylcinchonoyl-*m*-toluic acid, m.p. 180°, transformed by NH₃ into 2-phenylquinoline-4-carboxylamide, m.p. 195°. Piperazine 2-phenylquinoline-4-carboxylate has m.p. 203°. H. W.

Condensation of pyruvic acid with aromatic amines and aldehydes. IV. C. LEŚKIEWICZÓWNA and S. WEIL (Rocz. Chem., 1938, 18, 174—175).—*o*-Anisidine and AcCO₂H in EtOH (at the b.p.) condense with veratraldehyde, anisaldehyde, or 3-nitrovanillin, giving 8-methoxy-2-(3':4'-dimethoxyphenyl)-, +H₂O, m.p. 105—106°, -2-*p*-methoxyphenyl-, m.p. 203—204°, or -2-(2'-nitro-4'-hydroxy-3'-methoxyphenyl)-quinoline-4-carboxylic acid, m.p. 170—173° (decomp.). R. T.

Relationships between physicochemical properties and pharmacological action of alkoxyquinoline compounds.—See A., 1938, III, 688.

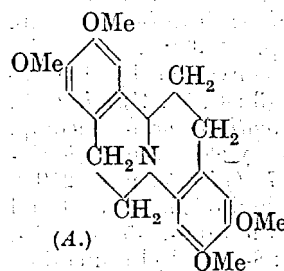
Isomerisation phenomena of 2-aminoindan-1:3-dione derivatives. G. WANAG and U. WALBE (Ber., 1938, 71, [B], 1448—1456).—2-Anilino-2-phenylindan-1:3-dione is converted by NaOMe in boiling MeOH into 1:4-diketo-2:3-diphenyl-1:2:3:4-tetrahydroisoquinoline, m.p. 156° (vac.), which passes when heated at 110° in an open vessel into phthalanil, m.p. 204°, and is transformed by acid into 1:4-diketo-3-phenylisochroman,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{CHPh} \\ \text{CO} \cdot \text{O} \end{smallmatrix}$, m.p. 148° (phenylhydrazone, m.p. 161°; *p*-nitrophenylhydrazone, m.p. 166—167°), which is reduced (Clemmensen) to dibenzyl-2-carboxylic acid and by Sn and 2N-HCl to 4-hydroxy-1-ketophenylisochroman, m.p. 162° (decomp.) when rapidly heated or m.p. 143—144° after softening at about 130° when slowly heated; this does not give CO-derivatives but is transformed by Ac₂O in C₅H₅N into the compound, C₁₅H₁₀O₂, m.p. 90°. 1:4-Diketo-3-phenyl-2-*p*-anisyl-, m.p. 181°, and -2-*p*-tolyl-, m.p. 183°, -1:2:3:4-

tetrahydroisoquinoline are obtained analogously. 2-Bromo-2-phenylindan-1:3-dione and CH₂Ph·NH₂ in Et₂O yield 2-benzylamino-2-phenylindan-1:3-dione, m.p. 109° (unstable hydrochloride; NO-derivative, m.p. 125°), transformed by NaOMe in boiling MeOH into 2-benzylamino-1:4-diketo-3-phenyl-1:2:3:4-tetrahydroisoquinoline, m.p. 132° (vac.) after softening, 2-iso-Butylamino-1:4-diketo-3-phenyl-1:2:3:4-tetrahydroisoquinoline has m.p. 118° (vac.). 2-Amino-2-phenylindan-1:3-dione, m.p. 99° (Ac derivative, m.p. 246°), gives 1:4-diketo-3-phenyl-1:2:3:4-tetrahydroisoquinoline, m.p. 257° after softening at 220°, transformed by NaOMe and MeI in boiling MeOH into the Me derivative, m.p. 240° after softening at 234°. 2-Anilino-2-methylindan-1:3-dione is converted into 1:4-diketo-2-phenyl-3-methyl-1:2:3:4-tetrahydroisoquinoline, m.p. 160—161° (vac.). 2-Bromo-2-methylindan-1:3-dione yields 2-*p*-toluidino-2-methylindan-1:3-dione, m.p. 163° (nitroso-2-*p*-toluidino-2-methylindan-1:3-dione, m.p. 183°), which gives 1:4-diketo-2-*p*-tolyl-3-methyl-1:2:3:4-tetrahydroisoquinoline, m.p. 157—158° (vac.). 2-*p*-Anisidino-2-methylindan-1:3-dione, m.p. 131°, affords 1:4-diketo-2-*p*-anisyl-3-methyl-1:2:3:4-tetrahydroisoquinoline, m.p. 162—163° (vac.). H. W.

Synthesis of dibenzopyridocoline derivatives.

I. Synthesis of 5:18-9:14-(2:3:11:12-tetramethoxy)dibenzo-6:7:15:6-tetrahydro-pyridocoline. S. SUGASAWA and K. KAKEMI (Proc. Imp. Acad. Tokyo, 1938, 14, 214—217).—The K derivative of 2-keto-6:7-dimethoxy-1:2:3:4-tetrahydroquinoline is converted by β-3:4-dimethoxyphenylethyl bromide and Cu powder in boiling xylene into 2-keto-6:7-dimethoxy-1-β-3':4'-dimethoxyphenylethyl-1:2:3:4-tetrahydroquinoline. This is transformed by POCl₃ in boiling PhMe into 5:18-9:14-(2:3:11:12-tetramethoxy)dibenzo-6:7:15:16-tetrahydro-8:17-dehydropyridocolinium chloride, decomp. 228° after changing colour at 220°, which is hydrogenated (PtO₂-Pt. black in EtOH) to 5:18-9:14-(2:3:11:12-tetramethoxy)dibenzo-6:7:15:16-tetrahydropyridocoline (A), m.p. 153—154° (methiodide, decomp. 237—238°; hydrochloride, decomp. 236—237°), identical with that derived from homo-



laudanoline. The yellowing of the free base in air is much accelerated if air is passed through the alcoholic solution containing Pt-black, whereby 5:18-9:14-(2:3:11:12-tetramethoxy)dibenzo-8:17-dehydropyridocolinium chloride, decomp. 231—232° (corresponding iodide, decomp. 279—280°), is produced; the last-named compound also results when the base is dehydrogenated by I in EtOH. H. W.

Dyes derived from thiohydantoin. III. G. P. PENNIE (J. Indian Chem. Soc., 1938, 15, 229—231).—Thiohydantoin condenses (position 5) with the following compounds in hot Ac₂O, yielding dyes having the m.p. given: phenanthraquinone, 146°; tetramethyldiaminobenzophenone, 166°; acenaphthenequinone, >260°; isatin, >260°; fluorenone, 102°; alizarin,

157°; benzil, 93°; dibenzylideneacetone, 113°; *p*-benzoquinone, 136°; anthraquinone, 167°.

A. L.

Simplified method of preparing histidine. L. E. GILSON (J. Biol. Chem., 1938, **124**, 281—285).—The method of Hanke and Koessler (A., 1920, i, 756) is simplified. Hæmoglobin hydrolysed by HCl is treated with NaOH, followed, after filtration, by H₂S or Na₂S. AcOH is added, followed by a relatively small amount of HgCl₂. Na₂CO₃ then ppt. the HgCl₂ salt of histidine, decomposed in aq. suspension by H₂S, giving the monohydrochloride of histidine, which is isolated as the dihydrochloride from a mixture of conc. HCl with 5 vols. of 80% dioxan. Full details are given.

E. W. W.

Condensation of phenylmethylpyrazolone derivatives with aromatic aldehydes. (A) J. JANICKA, C. HISZPAŃSKA, and S. WEIL. (B) W. DMOWSKA and S. WEIL (Rocz. Chem., 1938, **18**, 158—160, 170—173).—(A) 1-Aryl-3-methylpyrazol-5-one condenses with aldehydes, in EtOH–NaOH solution, to yield 4-*m*-nitro-, m.p. 176—177°, and 4-(3':4'-dimethoxybenzylidene)-1-*o*-tolyl-3-methylpyrazol-5-one, m.p. 222—223°, 4-*p*-dimethylaminobenzylidene-, m.p. 180°, 4-*p*-methoxybenzylidene-, m.p. 142°, 4-(4'-hydroxy-3'-methoxybenzylidene)-, m.p. 187°, and 4-(2'-nitro-4'-hydroxy-3'-methoxybenzylidene)-1-*p*-tolyl-3-methylpyrazol-5-one, m.p. 209°, and 4-(2'-nitro-4'-hydroxy-3'-methoxybenzylidene)-1-phenyl-3-methylpyrazol-5-one, m.p. 192°.

(B) 4-*p*-Dimethylamino-, m.p. 196°, and 4-*p*-nitrobenzylidene-1-phenyl-3-methylpyrazol-5-one, m.p. 209—210°, are prepared as above. With *m*-NO₂·C₆H₄·CHO the product of condensation is 4:4'-*m*-nitrobenzylidene-di-(1-phenyl-3-methylpyrazol-5-one) (I), m.p. 227—228°. This crystallises as a dihydrate from aq. EtOH, and the dihydrate loses H₂O at 100°, to yield an isomeric, presumably enolic, form of (I), m.p. 164—165°.

R. T.

2-Undecyl- and 2-heptadecyl-glyoxaline.—See B., 1938, 889.

Hydroxy-acids and their derivatives. VII. 2:5-Dialkylpiperazines. H. ŌEDA (Bull. Chem. Soc. Japan, 1938, **13**, 465—470).—The products obtained by hydrogenation of α-NH₂-amides and believed (A., 1937, II, 235, 456) to be (·CHR·CH₂·NH₂)₂ are identified as 2:5-dialkylpiperazines. Leucine anhydride and Na–EtOH give 2:5-diisobutylpiperazine, m.p. 80—83° [hydrochloride, m.p. >330°; (PhSO₂)₂ derivative, m.p. 211—213° (corr.); identical with the product from OH·CHBu^t·CO·NH₂], and a base (hydrochloride, m.p. 160—162°).

NH₂·CH(CH₂Ph)·CO₂Et, b.p. 135—136°/8 mm., and Na–EtOH give 2:5-dibenzylpiperazine, m.p. 166—167° (corr.) [Bz₂ derivative, m.p. 281—283° (corr.); identical with the product from OH·CPhMe·CO·NH₂], with *l*-, m.p. 92—94° (corr.), [α]_D²⁵ –24.4° in EtOH [Bz derivative, m.p. 169—171° (corr.)], and dl-β-amino-γ-phenylpropyl alcohol, m.p. 71—73° (corr.) [Bz derivative, m.p. 148—149° (corr.)].

R. S. C.

Pyrimidines. CLVIII. Oxidation of mercaptopyrimidines with chlorine water. T. B. JOHNSON and J. M. SPRAGUE (J. Amer. Chem. Soc.,

1938, **60**, 1622—1624).—2-Alkylthiopyrimidines and 4-hydroxy-2-alkylthiopyrimidines differ in their reaction with Cl₂ in H₂O or MeOH (cf. A., 1938, II, 30). Thus, passing Cl₂ into 4-amino-2-ethylthiol-5- or -6-methylpyrimidine and a little HCl in aq. MeOH gives 4-chloroamino-2-ethylsulphonyl-5- (I), m.p. 125—126°, and -6-methylpyrimidine, m.p. 133—134°, respectively. NaHSO₃ reduces (I) to 4-amino-2-ethylsulphonyl-5-methylpyrimidine, m.p. 136—137°. Similarly, 4-chloro-2-ethylthiol-6-methylpyrimidine gives 4-chloro-2-ethylsulphonyl-6-methylpyrimidine, b.p. 189—191°/3.5 mm., converted by cold NH₃–EtOH or hot aq. NH₃ into 4-chloro-2-amino-6-methylpyrimidine, m.p. 182—183°. 4-Hydroxy-2-ethylthiol-5-methylpyrimidine in MeOH gives 5-chloro-2:4-diketo-6-methoxy-5-methylhexahydropyrimidine, m.p. 220—221°, reduced by HI to “thymine.” 4-Hydroxy-2-ethylthiol-6-methylpyrimidine gives 5:5-dichloro-2:4-diketo-6-methoxy-6-methyltetrahydropyrimidine, m.p. 274—275° (decomp.), reduced by Sn–HCl to 5-chloro-6-methyluracil, and 6-hydroxy-2-methyl- or -ethyl-thiopyrimidine gives 5:5-dichloro-2:4-diketo-6-methoxytetrahydropyrimidine, m.p. 225—226°.

R. S. C.

Attempted synthesis of methylenediquinazolone derivatives. A. KASSUR and S. WEIL (Rocz. Chem., 1938, **18**, 163—169).—CH₂(CO·NH₂)₂ or NH₂·CO·CH₂·CO·NHPh and *o*-NH₂·C₆H₄·CO₂H (I) (4—5 hr. at 150—155°) yield CH₂(CO·NHPh)₂ (II). Et malon-*p*-anisidide (III) and (I) (4—5 hr. at 160°) afford CH₂(CO·NH·C₆H₄·OMe)₂ (IV). Et malon-*p*-toluidide and (I) (5 hr. at 160°) give the substance, C₆H₄ < $\begin{matrix} \text{CO} \cdot \text{NR}' \\ \text{N} = \text{CR} \end{matrix}$ (R = CH₂·CO·NH·C₆H₄Me; R' = *p*-C₆H₄·CO₂H), m.p. 218—219°. In presence of POCl₃ (I) condenses with NHPhAc, to yield 3-phenyl-methylquinazol-4-one, with phenacetin to give 3-*p*-phenetyl-2-methylquinazol-4-one, and with (IV) to give “methylenedi-(*p*-methoxyphenyl)quinazolone,” m.p. <310°. PhCHO and (II) in EtOH and Na (24 hr. at the b.p.) give a condensation product, m.p. 242—243°, of 1 mol. of PhCHO with 2 mols. of (II). *o*-OH·C₆H₄·CHO condenses with malon-*o*-toluidide or (III) in presence of piperidine, to give coumarin-3-carboxy-*o*-toluidide or -*p*-anisidide, m.p. 214°.

R. T.

Formation of 2- and 3-3'-pyridylpyrrole by the thermal decomposition of 1-3'-pyridylpyrrole. J. P. WIBAUT and H. P. L. GITSELS (Rec. trav. chim., 1938, **57**, 755—760).—Passage of 1-3'-pyridylpyrrole through a tube at 710—720° gives 3-, m.p. 137.5°, b.p. 160°/0.2 mm. [monopicrate, m.p. 199°; picrolonate, m.p. 254—255° (decomp.); 1-Me derivative (picrate, m.p. 194.5—195.5°)], and 2-3'-pyridylpyrrole (I), m.p. 100—100.8° [picrate, m.p. 202—203°; picrolonate, m.p. 250° (decomp.)]; K–Mel in PhMe gives β-nicotyrine. The product, m.p. 72°, of Pictet *et al.* (A., 1895, i, 627), supposed to be (I), was thus a mixture, and the structural significance of their synthesis of nicotine disappears.

R. S. C.

Reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. XVIII. 1:4-Diketo-3-(aminoaryl)tetrahydrophthalazines and related compounds. F. M. ROWE, M. A.

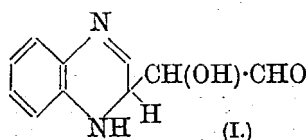
LÉCUTIER, and A. T. PETERS (J.C.S., 1938, 1079—1083).—The methods by which 1:4-diketo-3-(nitro-aryl)tetrahydrophthalazines and 4-keto-1-methoxy-3-(nitroaryl)-3:4-dihydrophthalazines have been obtained are reviewed. 4-Keto-1-methoxy-3-(4'-aminophenyl)-3:4-dihydrophthalazine, m.p. 197°, obtained by reduction ($\text{Na}_2\text{S}_2\text{O}_4$) of the NO_2 -compound, is deaminated to the 3-Ph derivative, and 1:4-diketo-3-(4'-aminophenyl)tetrahydrophthalazine ($+\text{H}_2\text{O}$), m.p. 247—248° (N-Ac derivative, m.p. 299—300°), and the 3'-aminophenyl compound, m.p. 233—234° [N-Ac derivative ($+\text{H}_2\text{O}$), m.p. 153—154°], are similarly prepared. Reduction of the NO_2 -compounds with $\text{SnCl}_2\text{--HCl}$ affords 4-keto-1-methoxy-3-(3'-aminophenyl)-3:4-dihydrophthalazine, m.p. 181° (Ac derivative, m.p. 246—247°), and the 2'-aminophenyl compound, m.p. 234—235° (Ac derivative, m.p. 219—220°), and 1:4-diketo-3-(2'-aminophenyl)tetrahydrophthalazine ($+\text{C}_5\text{H}_5\text{N}$), m.p. 430° (decomp.) (Ac_2 derivative, m.p. 224—225°), converted by heating into 2':4-anhydro-1:4-diketo-3-(2'-aminophenyl)tetrahydrophthalazine, m.p. $>430^\circ$ (decomp.) (O-Ac derivative, m.p. 222—223°). 4-Keto-1-methoxy-3-(4'-chloro-2'-nitrophenyl)-3:4-dihydrophthalazine, m.p. 225—228°, is reduced (Fe--AcOH) to the --NH_2 -compound, m.p. 217—219° (Ac derivative, m.p. 272—274°). 1:4-Diketo-3-(4'-chloro-2'-aminophenyl)-tetrahydrophthalazine, m.p. $>440^\circ$ (Ac_2 derivative, m.p. 245—246°), obtained by reduction (SnCl_2) of the --NO_2 -compound, m.p. 286—287°, gives the 2':4-anhydro-derivative, m.p. $>440^\circ$ (O-Ac derivative, m.p. $>440^\circ$), on heating. F. R. S.

Amino-alcohols derived from carbazole. L. RUBERG and L. SMALL (J. Amer. Chem. Soc., 1938, 60, 1591—1593).—2-Acetyl-9-methylcarbazole (prep. in 77% yield from 1:9-diacetylcarbazole, Me_2SO_4 , and KOH in aq. COMe_2) (1 mol.), $(\text{CH}_2\text{O})_3$ (2.5 mols.), and the appropriate amine hydrochloride (1.2 mol.) in $\text{iso-C}_5\text{H}_{11}\text{OH}$ give 2- β -dimethylamino-, m.p. 111.5—113.5° (hydrochloride, m.p. 191.5—193°), -diethylamino-, m.p. 70.5—72.5° (sinters at 69°) [hydrochloride, m.p. 163.5—166° (sinters at 160°)], and -1':2':3':4'-tetrahydroisoquinolino-propionyl-9-methylcarbazole, m.p. 123—125° [hydrochloride, m.p. 211—213° (sinters at 209°)], hydrogenated (PtO_2) to 9-methyl-2- γ -dimethylamino-, m.p. 96.5—99° [hydrochloride, m.p. 195—196.2°; p-nitrobenzoate hydrochloride, m.p. 165—166.5° (softens at 164°)], -diethylamino- (I), m.p. 75.2—76° (sinters at 73°) [picrate, m.p. 136—138.5°; p-nitrobenzoate hydrochloride, m.p. 179—180.5° (sinters at 177°); decomposed by HCl--EtOH], and -1':2':3':4'-tetrahydroisoquinolino- α -hydroxy-n-propylcarbazole, m.p. 151.5—153° [decomposed by HCl--EtOH ; styphnate, m.p. 171—175° (decomp.; sinters at $>135^\circ$); p-nitrobenzoate hydrochloride, m.p. 159.5—161° (sinters at 153°)]. Use of impure material in the prep. of (I) leads to a substance, m.p. 133—135° (oxime, m.p. 172—173°). 1-Keto-9-methyl-1:2:3:4-tetrahydrocarbazole, m.p. 101.5—103.5°, with $(\text{CH}_2\text{O})_3$ and NHMe_2HCl gives 1-keto-9-methyl-2-dimethylaminomethyl-1:2:3:4-tetrahydrocarbazole, m.p. 74—75° (sinters at 72.5°) [hydrochloride, m.p. about 190° (decomp.; sinters at about 180°)], hydrogenated to 1-hydroxy-9-methyl-2-

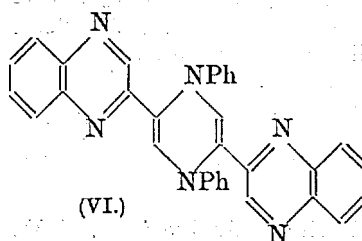
dimethylaminomethyl-1:2:3:4-tetrahydrocarbazole, m.p. 123.5—125°, which is dehydrated by HCl--EtOH to (?) 9-methyl-2-dimethylaminomethyl-3:4-dihydrocarbazole hydrochloride, m.p. 192—194° (decomp.; sinters at about 180°). (I) approaches codeine in analgesic action, but has a convulsant effect; it shows the Straub tail-reaction of morphine in mice.

R. S. C.

Alkaline degradation of tetrahydroxybutylquinoxaline and new quinoxaline derivatives. K. MAURER and B. BOETTGER (Ber., 1938, 71, [B], 1383—1391).—Tetrahydroxybutylquinoxaline is transformed by NaOMe in warm $\text{MeOH--C}_5\text{H}_5\text{N}$ mainly

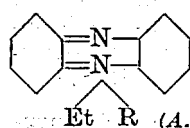


into the red amorphous 1:2-dihydroquinoxalylglycollaldehyde (I), m.p. 138—144° (decomp.), the constitution of which is established by its conversion by NHPh--NH_2 into quinoxalylglyoxalphenylosazone (II), $\text{C}_{22}\text{H}_{18}\text{N}_6$, m.p. 243°, and by $\text{Ac}_2\text{O--C}_5\text{H}_5\text{N}$ into quinoxalylglycollaldehyde acetate, m.p. 117°, which immediately reduces cold Fehling's solution. Alkaline oxidation of (I) affords quinoxaline-2-carboxylic acid (III), m.p. 210°. Short treatment of (I) with boiling NH_2Ph gives 1:2-dihydroquinoxalylglycollaldehydeanil (IV), m.p. 188°, converted by excess of NHPh--NH_2 in hot EtOH into (II) and by boiling Ac_2O into the acetate (V), $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}_3$, m.p. 134°; it is oxidised by O_2 in presence of alkali to (III) and PhNC . Dehydrogenation of (IV) by H_2O_2 in PhMe gives quinoxalylglycollaldehydeanil, m.p. 208°, converted by NHPh--NH_2 into (II) and by Ac_2O in boiling $\text{C}_5\text{H}_5\text{N}$ into (V). The constitution of (IV) is further



established by its gradual transformation into the pyrazine derivative (VI), m.p. 253°. 1:2-Dihydroquinoxalylglycollaldehyde-p-tolil, m.p. 150°, is readily transformed into the corresponding dehydro-compound, m.p. 190°, and affords a pyrazine derivative, $\text{C}_{34}\text{H}_{26}\text{N}_6$, m.p. 267°. The xylil, m.p. 106°, its dehydro-compound, m.p. 187°, and the pyrazine derivative, m.p. 276°, are described. (III) (improved prep.) gives a Fe^{II} and an aniline, m.p. 156°, salt. Quinoxaline-2-carboxyl chloride, m.p. 115°, from (III) and SOCl_2 , yields the corresponding anilide, m.p. 180°, p-toluidide, m.p. 150°, m-4-xylidide, m.p. 132°, and Et ester, m.p. 85°. Tetrahydroquinoxaline-2-carboxanilide has m.p. 154°. H. W.

Flavinduline derivatives. VIII. K. YAMADA and N. HASEBE (J. Soc. Chem. Ind. Japan, 1938, 41, 160—161b).—The solubility, colour reactions, dyeing



properties, and fastness of the dyes (A; $\text{R} = \text{Cl} + 0.5\text{ZnCl}_2$, m.p. 209—211°; $\text{R} = \text{Br}$, m.p. 220—222°; $\text{R} = \text{I}$, m.p. 128—130°) derived from p-benzoquinone (I) and o- $\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2$ are described. The similar dyes from phenanthraquinone [chloride ($+0.5$

ZnCl_2 , m.p. 206—208°; bromide, m.p. 218—220°; iodide, m.p. 154—156°] have been prepared.

H. W.

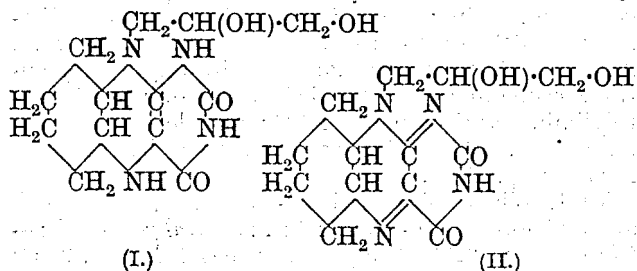
Pyrimidines.—See B., 1938, 889.

Triazines. II. Lactim-lactam isomerism in substituted tetrahydrotriazines. (MISS) E. BLOCH and H. SOBOTKA (J. Amer. Chem. Soc., 1938, 60, 1656—1658; cf. A., 1938, II, 70).—Benzoylbiuret (modified prep.), m.p. 214—216°, is converted by KOH into 4:6-diketo-2-phenyl-3:4:5:6-tetrahydrobiuret, m.p. 297—300°. This is dimethylated by CH_2N_2 in dry Et_2O partly at the two sec. N and partly at the N in position 3 and the enolic form of the CO at 6, giving 4:6-diketo-2-phenyl-3:5-dimethyl-3:4:5:6-tetrahydrotriazine (I), m.p. 132°, and 4-keto-6-methoxy-2-phenyl-3-methyl-3:4-dihydrotriazine (II), m.p. 183°. With 25% NaOH (I) gives BzOH, NH_3 , and >1 mol. of NH_2Me ; with Br it gives a cryst. Br_4 -derivative, unstable in air, Et_2O , or aq. alkali or in presence of Ag salts. With 2N-NaOH or aq. or alcoholic HCl (II) gives 4:6-diketo-2-phenyl-3-methyl-3:4:5:6-tetrahydrotriazine, m.p. 278—280°, which could not be converted into (I), but with CH_2N_2 gives 80% of (II). M.p. are corr. R. S. C.

Absorption of light and tautomerism of uric acid and cyanuric acid. E. AGALLIDIS, H. FROMHERZ, and A. HARTMANN (Ber., 1938, 71, [B], 1391—1398).—It is not possible to maintain the arguments advanced by Biltz (cf. A., 1937, II, 78) against the author's conception, based on measurements of the absorption of light, that uric acid and its salts invariably exist in the keto- (lactam) -form even in alkaline solution. It is shown in the case of cyanuric acid (I), which exists in a keto-form in acid and a OH-form in alkaline solution, that a keto-enolic equilibrium of this type can be very readily detected by its light absorption curve. In the practically saturated aq. solution of (I), 5.6% of the OH-form is present.

H. W.

Octahydroflavins. P. KARRER and R. OSTWALD (Rec. trav. chim., 1938, 57, 500—502).—In presence of PtO_2 9- $\beta\gamma$ -dihydroxy-*n*-propylisoalloxazine in H_2O absorbs 4 H_2 to give the H_8 -derivatives (I), decomp. 255—260° (yellowish-green fluorescence in ultra-violet light), oxidised in alkaline solution to the H_6 -



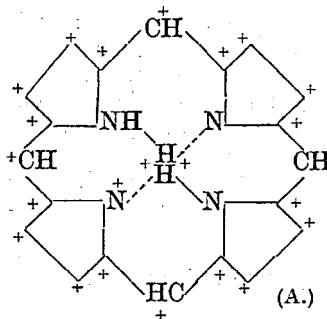
derivative (II), decomp. about 263° (violet-blue fluorescence in ultra-violet light). 9-Hydroxyethyl- and 9-*d*-arabityl-isoalloxazine, but not lactoflavin, give similar H_8 -derivatives; the effect of Me in positions 6 and 7 is evident. R. S. C.

Lactoflavinphosphoric acid-adeninenucleotide from liver and the co-enzyme of *d*-alaninedehydrogenase. P. KARRER, P. FREI, B. H. RINGIER,

and H. BENDAS (Helv. Chim. Acta, 1938, 21, 826—828).—A prep. of lactoflavinphosphoric acid-adeninenucleotide (I) from liver was able to activate *d*-alaninedehydrogenase, but the property was lost after further purification of (I). H. W.

Photoluminescent properties of synthetic flavin.—See A., 1938, I, 435.

Porphyrins and their metallic salts. V. Absorption and fluorescence of porphyrins in different solvents and the detailed structure of the porphin ring. F. HAUROWITZ [with F. KRAUS and G. APPEL] (Ber., 1938, 71, [B], 1404—1412).—The absorption spectra of dimethylmesoporphyrin (I) and tetramethylhaematoporphyrin in 3l media and certain acids and the fluorescence have been measured. Replacement of hexane by polar solvents causes a displacement of band I (in red) towards shorter λ and of the max. of band IV (in blue) towards longer λ . In the non-polar solvents CCl_4 and CS_2 all the visible absorption bands are displaced towards the red. Displacement of the absorption max. by polar solvents is not accompanied by marked spreading or depression thereof. Only in the alcohols, MeOH to $\text{C}_5\text{H}_{11}\cdot\text{OH}$, do the bands become less defined so that the max. of the weak band 1a can no longer be accurately measured. Apparently, therefore, the chromophoric groups of the porphyrins are not



immediately accessible to the solvent mols. and solvation does not occur. In mineral acids salt formation and true solvation of the chromophoric basic N-containing groups must be assumed. The fluorescence of the porphyrins is extinguished by MeI and CHBr_3 and greatly

weakened by $\text{C}_2\text{H}_4\text{Br}_2$. In spite of their numerous double linkings porphyrins behave as aromatic and not as unsaturated olefinic compounds. They are not hydrogenated by $\text{Na}_2\text{S}_2\text{O}_4$ or by H_2 -Pd-asbestos in alkaline solution. Their perbromides are readily converted by loss of Br into the initial materials. The absorption spectrum of mesoporphyrin ester hydrochloride in CHCl_3 is not considerably affected by SbCl_3 . (I) is unchanged by molten maleic anhydride. The intimate structure of the porphyrin ring is, therefore, best expressed by A. H. W.

Behaviour of chlorophyll derivatives towards chlorophyllase. H. FISCHER and R. LAMBRECHT (Z. physiol. Chem., 1938, 253, 253—260).—Chlorophyllase (I) catalyses the esterification of phaeophorbide-*a* and -*b* and of the corresponding meso-compounds with MeOH and EtOH but does not cause ring-cleavage or enable Mg to enter into complex combination. It does not catalyse the esterification of pyropheophorbide-*a*, of phaeoporphyrin-*a*₅, of other porphyrins, or of haemin but it removes Me from the Me_3 ester of purpurin-7 [yielding the corresponding Me_2 ester (+0.5 H_2O), m.p. 225°] and from the Me_3

ester of mesopurpurin-7 and hydrolyses the Me ester of mesopurpurin-18. (I) also causes other changes in the constitution of the *meso*-compounds. Chlorins of the chlorophyll and the bacteriochlorophyll series are not affected by (I). The $[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$, the CO_2H at 10, and the H at $\text{C}_{(5)}$ and $\text{C}_{(6)}$ in chlorophyll and its derivatives have a decisive effect on the action of (I).

W. McC.

(A) Coupled oxidation of ascorbic acid and hæmochromogens. (B) Chemical mechanism of the oxidation of protohæmatin to verdohæmatin. R. LEMBERG, B. CORTIS-JONES, and M. NORRIE (Biochem. J., 1938, **32**, 149—170, 171—186; cf. A., 1937, III, 364).—(A) The coupled oxidation of $\text{C}_5\text{H}_5\text{N}$ -hæmochromogen and ascorbic acid (I) by atm. O_2 results in the oxidation of 0.2 mg. of hæmatin (II) and 1 mg. of (I). Verdohæmochromogen (III) is the only oxidation product of (II) and catalyses the oxidation of (I), from which the main oxidation product is dehydroascorbic acid. Oxidation of (II) is more affected by temp. variation than that of (I). The oxidation of (I) \propto the O_2 tension whilst that of (II) is little affected. NaCN inhibits the reaction to an extent depending on the (I) concn. Glutathione preserves (I) by back-reduction of its oxidation product, (I) acting as H-carrier between (II) and glutathione.

(B) In the formation of (III) from $\text{C}_5\text{H}_5\text{N}$ -hæmochromogen an intermediate hæmatin compound (IV) with an absorption band at 639 m μ . is formed; it is oxidised by atm. O_2 to (III). Protohæmochromogen yields (IV) with H_2O_2 ; the reaction is prevented by catalase. (I) is oxidised by an independent mechanism involving Fe^{+++} hæmochromogen. (I) may be replaced by cysteine in the presence of Cu or Fe, but not by glutathione with or without metal. The mechanism of "green pigment" and methæmoglobin formation is discussed.

J. L. C.

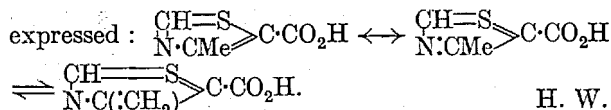
Absorption spectra of pyrrole dyes. II.—See A., 1938, I, 432.

Fluorescence of the chlorins.—See A., 1938, I, 434.

Preparation of 3-keto-8-carboxy-2-methyl-3:4-dihydro-1:4-benzoxazine. H. W. COLES and W. G. CHRISTIANSEN (J. Amer. Chem. Soc., 1938, **60**, 1627—1628).—3:2:1- $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$ and $\text{CHMeBr}\cdot\text{COBr}$ in C_6H_6 give 3- α -bromopropionamidosalicylic acid, m.p. 188° (corr.) (sinters at 178°); converted by 10% NaOH at 60° into 3-keto-2-methyl-3:4-dihydro-1:4-benzoxazine-8-carboxylic acid, m.p. 285° (corr.), which has no antipyretic or hypnotic action.

R. S. C.

Structure of thiazole. H. ERLÉNMEYER and H. M. WEBER (Helv. Chim. Acta, 1938, **21**, 863—866).—4-Methylthiazole-5-carboxylic acid (I) suspended in D_2O is neutralised by NaOD; after 3 hr. at room temp. the solution is acidified with D_2SO_4 , when 4 H of (I) are found to have been replaced by 4 D. An analogous behaviour is not shown by $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$. A tautomeric equilibrium which is not expressed by the usual formula is thus necessitated for (I). This and the aromatic character of S are



H. W.

Properties of isosteric and structurally similar compounds. VII. Preparation of 3-hydroxybenzthiazole. H. ERLÉNMEYER, H. UEBERWASSER, and H. M. WEBER (Helv. Chim. Acta, 1938, **21**, 709—711).—Boiling $o\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CHO}$ is transformed by S into 3-methoxy-1-thiolbenzthiazole, m.p. 208°, oxidised by NaOCl to 3-methoxybenzthiazole-1-sulphonic acid (Na and K salts). This is converted by Na-Hg and 50% H_2SO_4 into 3-methoxybenzthiazole, m.p. 103°, transformed by boiling conc. HI or 48% HBr into 3-hydroxybenzthiazole, m.p. 143°.

H. W.

Constitution of the so-called dithiourazole of Martin Freund. Ring-closure of hydrazodithiocarbonamide and its mono- and di-substituted derivatives. VII. Action of heat. VIII. Action of sodium hydroxide. IX. Action of hydrochloric acid. X. Action of acetic anhydride. P. C. GUHA and D. R. MEHTA. XI. Isomeric changes of some triazoles and thiodiazoles. P. C. GUHA and S. L. JANNIAH (J. Indian Inst. Sci., 1938, **21**, A, 41—59, 60—64; cf. A., 1933, 726).—VII. Hydrazodithiocarbonamide at 210—215° yields 3-imino-5-thiontetrahydro-1:2:4-triazole. Similarly phenyl-, o -tolyl-, (I), and p -tolyl-hydrazodithiocarbonamide (II) at 180—185° yield respectively 3-imino-5-thion-4-phenyltetrahydro-1:2:4-triazole, 3-imino-5-thion-4- o -, (III), m.p. 231° (acetate, m.p. 205°; Me derivative, by $\text{Me}_2\text{SO}_4\text{--NaOH}$, m.p. 142°), and -4- p -tolyltetrahydro-1:2:4-triazole, m.p. 277° (IV) (acetate, m.p. 160°; Me derivative, m.p. 142°). Diphenylhydrazodithiocarbonamide at 180° yields 5-anilo-3-thion- and 3:5-diphenylimino-tetrahydro-4:2:1-thiodiazole, whilst above 200° an alkali-sol. product, m.p. 206°, and alkali-insol. product, m.p. 232—233° (acetate, m.p. 174°), are formed. Similarly, di- o -tolylhydrazodithiocarbonamide (V) at 170° yields 3-thion-5-imino-5- o -tolyltetrahydro-4:1:2-thiodiazole, (VI), m.p. 213—214° [disulphide, by oxidation with I, m.p. 200°; Me derivative, by MeI--MeOH--KOH , m.p. 158° (acetate, m.p. 123°); CH_2Ph derivative, by CH_2PhCl in EtOH--KOH , m.p. 112—113°; acetate, m.p. 249°; diacetate, m.p. 145°], and 3:5-di- o -tolyliminotetrahydro-4:1:2-thiodiazole (VII), m.p. 217° [acetate (IX), m.p. 251°]. Di- p -tolylhydrazodithiocarbonamide (VIII) at 185° yields only 3:5-di- p -tolyliminotetrahydro-4:1:2-thiodiazole (X) [acetate (XI), m.p. 166—167°; azo-derivative, by $\text{KMnO}_4\text{--AcOH}$, m.p. 167°].

VIII. When boiled with 2N-NaOH, (I) yields (III) and 3:5-dithion-4- o -tolyl-2:3:4:5-tetrahydro-1:2:4-triazole, m.p. 223° (disulphide, by KOH--I , m.p. 245°; Me_2 derivative, m.p. 178°), whilst (II), similarly treated, yields (IV) and 3:5-dithion-4- p -tolyl-2:3:4:5-tetrahydro-1:2:4-triazole, m.p. 213° [disulphide, m.p. 227° (decomp.); Me_2 derivative, m.p. 140°].

IX. When heated with conc. HCl for 30 min. (V) yields (VI) and (VII) whilst (VIII) yields 5- p -tolylimino-3-thiontetrahydro-4:1:2-thiodiazole.

X. When heated with Ac_2O , (I) yields the acetate,

m.p. 265°, of 5-*o*-tolyliminotetrahydro-4:1:2-thiodiazole, m.p. 206–207°, whilst (II) yields the acetate, m.p. 298°, of 5-*p*-tolyliminotetrahydro-4:1:2-thiodiazole, m.p. 188°. With (V), Ac_2O yields (IX), which is hydrolysed (HCl) to 2:3 dihydro-3-*o*-tolylamino-3:5-endo-*o*-tolylimino-4:1:2-thiodiazole, m.p. 223°; similar treatment of (VIII) yields (XI), hydrolysed to (X).

XI. With Ac_2O , 3:5-dithiol-4:1:2-thiodiazole yields di-(3-thiol-2:4:5-thiodiazole) sulphide, m.p. 180° (dibenzyl derivative, m.p. 107°), whilst 3:5-dithiol-4:2:1-triazole yields the diacetate, m.p. 330°, which is hydrolysed (HCl) to a substance, $\text{C}_2\text{H}_3\text{N}_3\text{S}_2$, m.p. 228°, probably either 5-imino-3-thiol-4:1:2-thiodiazole or 3-thiol-3:5-endothio-2:3-dihydro-1:2:4-triazole. 3:5-Dithiol-4-phenyl-1:3:4-triazole when heated with HCl yields 3-thion-5-anilotetrahydro-4:1:2-thiodiazole. J. D. R.

New heterocyclic syntheses. II. Reactions with halogeno-oximes. C. MUSANTE (Gazzetta, 1938, 68, 331–342).— $\text{NH}_2\text{CPhNH}_2\cdot\text{HCl}$ (I) in $\text{MeOH}-\text{NaOMe}$ with $\text{CPhClN}\cdot\text{OH}$ (II) yields 3:5-diphenyl-1:2:4-oxadiazole. With KCNO in aq. EtOH , (II) gives 3-phenyl-1:2:4-oxadiazol-5-one. With NH_4CNS in aq. EtOH , 2-imino-4-phenyl-1:3:5-oxathiazole (III), m.p. 82–84°, is formed, which is readily (e.g., by steam-distillation) converted into 4-phenyl-1:3:5-oxathiazol-2-one ureide (IV), m.p. 165–166°, and PhNCS , which is also obtained, with N_2 and CO_2 , from (III) and HNO_2 , or from (IV) and boiling aq. HCl. With (I) and $\text{MeOH}-\text{NaOMe}$, $\text{CO}_2\text{Et}\cdot\text{CClN}\cdot\text{OH}$ gives the *Et* ester, m.p. 110–111°, of 5-phenyl-1:2:4-oxadiazole-3-carboxylic acid (cf. A., 1912, i, 724), m.p. 119–120° (decomp. to benzoylcyanamide). Using excess of (I), a product, m.p. 172° is obtained. Structures and mechanisms are discussed. E. W. W.

8-Methyl-2:2'-diethyloxa-thia-[-seleno-]carbocyanine iodide.—See B., 1938, 984.

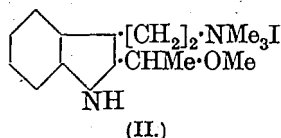
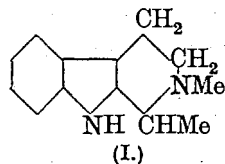
Calycanthidine, a new simple indole alkaloid. G. BARGER, (MISS) A. JACOB, and J. MADINAVETIA (Rec. trav. chim., 1938, 57, 548–554).—The seeds (45 kg.) of *Calycanthus floridus* yield, besides calycanthine (probably contains 2 tryptophan nuclei), calycanthidine (I) (12 g.), $\text{C}_{13}\text{H}_{16}\text{N}_2$, m.p. 142°, $[\alpha]_D^{20}$ –285.1° in MeOH (hydriodide, m.p. 182°; perchlorate, m.p. 158°; platinichloride, m.p. 198–200° after sintering at 175°; picrate, m.p. 192°; chromate, m.p. >300°), the methiodide, m.p. 180–215°, of which with $\text{MeI}-\text{MeOH}-\text{KOH}$ or $-\text{K}_2\text{CO}_3$ gives a salt (II), $\text{OMe}\cdot\text{C}_{12}\text{H}_{23}\text{N}\cdot\text{NMe}_3\text{I}$, m.p. 221°, also obtained similarly directly from (I). With $\text{Ag}_2\text{O}-\text{MeOH}$ the methiodide gives NMe_3 and an oily compound, b.p. 120–160°/14 mm. (hydrochloride, amorphous, m.p. 135–137° (sinters at 107°); gives a pink colour with *p*-

converted reversibly by heat into a claret colour. (I) contains NMe and possibly CMe . (I) and (II) may have the formulæ shown. However, (I) and dil. $\text{HCl}-\text{HNO}_2$ give in the cold a neutral, yellow ppt. (resinified by an excess of HNO_2), given by dl-*N*-methyltetrahydroharman (III) only when heated (then unaffected by an excess of HNO_2), and determination of CMe in (I) gives a very low, in (III) a fair, result. Further, (III) with $\text{MeI}-\text{K}_2\text{CO}_3-\text{MeOH}$ gives a normal methiodide, m.p. 228–229°. (III), obtained from *N*-methyltryptamine and MeCHO in 0.25*N*- H_2SO_4 at 50–100°, has m.p. 112° and could not be resolved by way of the *l*-malate, m.p. 239°, $[\alpha]_D^{20}$ –2.2° in MeOH , or *d*-camphorsulphonate, m.p. 229°, $[\alpha]_D^{20}$ +24.2° in MeOH . Conversely, attempts to racemise (I) failed. R. S. C.

isoQuinoline and other alkaloids. G. BARGER (Congr. Int. Quim. pura apl., 1934, 9, IV, 97–122; Chem. Zentr., 1936, ii, 2727).—The investigation of the metabolism of higher plants by comparing the structures of plant constituents (alkaloids) is recalled with reference to the isoquinoline group. It is shown that (with the accompanying numbering) benzylisoquinolines may be obtained by ring-closure through 6:β':N, the aporphines by a second ring-closure through 6:2' (leading to 3':4' derivatives) or 6:6' (4':5'-derivatives), and the berberine group by a second ring-closure through N and an additional C (from CH_2O ?). 70 alkaloids as well as those of the indole group are considered. A. H. C.

Alkaloids of fumariaceous plants. XVII. Corydalis caseana, A. Gray. R. H. F. MANSKE and M. R. MILLER (Canad. J. Res., 1938, B, 16, 153–157; cf. A., 1931, 764).—The method of separation is as described previously (cf. A., 1933, 728). The following are new: caseanine, $\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}$, m.p. 142° (+ H_2O , m.p. 115–116°; picrate, m.p. 112–113°, identical with aurotensine Me_2 ether picrate); a dimethoxy-phenolic compound, $\text{C}_{19}\text{H}_{21}\text{O}_4\text{N}$, m.p. 257° (previous darkening); casealutine, $\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}$, m.p. 230° (converted by CH_2N_2 into caseanine), and isomerides, m.p. 218° after sintering some degrees lower, and 145° (*OMe*-derivative, m.p. 186°), respectively. J. L. D.

Alkaloids of Lycopodium clavatum, L. O. ACHMATOWICZ and W. UZIĘBŁO (Rocz. Chem., 1938, 18, 88–95).—*L. clavatum* plants contain 0.12% dry wt. of alkaloids, of which 40% are crystallisable, and consist of 83% of lycopodine, $\text{C}_{16}\text{H}_{25}\text{ON}$, m.p. 115–116°, $[\alpha]_D^{20}$ –9.01° in COMe_2 (methiodide, m.p. 335–337°; methochloride, m.p. 238–240°), 12% of clavatine, $\text{C}_{16}\text{H}_{25}\text{O}_2\text{N}$, m.p. 212–213°, $[\alpha]_D^{20}$ –365.7° in COMe_2 (methiodide, m.p. 317–318°), and 3% of clavotoxine, $\text{C}_{17}\text{H}_{27}\text{O}_2\text{N}$, m.p. 185–186°. The alkaloids do not contain NMe or OMe . They give characteristic colour reactions with the usual alkaloid reagents. All are physiologically active, stimulating the respiratory centre of mammals, and paralysing the central and peripheral nervous systems of frogs. R. T.

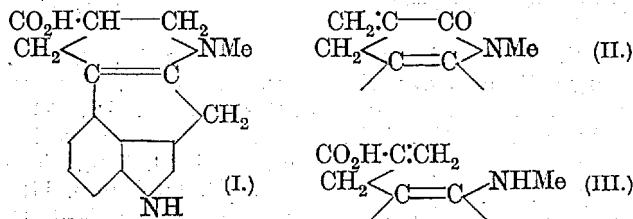


$\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$; unaffected by H_2-PtO_2 . With Ehrlich's reagent (I) gives a pale yellow colour,

Lycoris alkaloids. XIII. N-Isomerism of lycorine methiodide. H. KONDO, H. KATSURA, and S. UYEO (Ber., 1938, **71**, [B], 1529—1533).—Treatment of lycorine with MeI gives the α -methiodide (I), m.p. 247° (decomp.), $[\alpha]_D^{25} -46.11^\circ$ in H_2O , and the β -methiodide (II), m.p. 281° (decomp.) [*monohydrate*, m.p. 198° (decomp.), $[\alpha]_D^{25} +122.9^\circ$ in $H_2O \equiv [\alpha]_D^{25} +128.1^\circ$ for the anhyd. material]. The Hofmann degradation of either compound leads to the same methine base, m.p. 98.5° [*hydrochloride*, m.p. 214—215° (decomp.)]. The Emde degradation of lycorine α -methochloride, $C_{16}H_{17}O_4N, MeCl, 2H_2O$, leads to a methine base, $C_{15}H_{17}O_2N$, m.p. 71—71.5° [*picrate*, m.p. 197—198° (decomp.)], also obtained from lycorine β -methochloride, m.p. 305° (decomp.). The stereoisomerism of (I) and (II) is therefore due to co-ordinatively quadrivalent N. H. W.

Acidimetric titration of ergometrine. F. REIMERS (Quart. J. Pharm., 1938, **11**, 252—259).—The presence of ergotoxine, ergotinine, and ergotamine in ergometrine (I) can be shown by pptn. of the former with picric acid. Ergometrine can be determined by titration with 0.1N-HCl (macro-method) or 0.02N-HCl (micro-method) using bromophenol-blue as indicator. In the micro-method the error is $\pm 0.2\%$. K_{acid} and K_{base} for (I) at approx. 22° are $10^{-6.80}$ and $10^{-7.28}$ respectively. J. N. A.

Position of the carboxyl group in lysergic acid. W. A. JACOBS and L. C. CRAIG (J. Amer. Chem. Soc., 1938, **60**, 1701—1702).—At 300°/25 mm. dihydrolysergic acid (I) partly sublimes unchanged and partly yields a neutral substance (II), $C_{16}H_{16}ON_2$, m.p. 305—307° (decomp.), $[\alpha]_D^{25} -219^\circ$ in C_5H_5N (obtained in



33% yield at 350°), hydrogenated to the H_2 -derivative, m.p. 336° (decomp.). Thus (I) and (II) have the formulæ shown, (I) being a β - NH_2 -acid (in accordance with unpublished data on dissociation const.) and yielding (II) by way of (III). R. S. C.

Chemistry and biochemistry of the alkaloids related to tryptophan. G. BARGER (Bull. Soc. Chim. biol., 1938, **20**, 685—704).—A lecture.

Conversion of colchicine into colchiceine. E. BOYLAND and E. H. MAWSON (Biochem. J., 1938, **32**, 1204—1206).—The colorimetric determination of colchiceine (I), based on the development of a green colour with $FeCl_3$ in $CHCl_3$, is described. Colchicine is hydrolysed to (I) (93%) by heating for 1 hr. at 100° with 0.1N-HCl. P. G. M.

α -Phenylcinchononitrile. T. LIPIEC and S. WEIL (Rocz. Chem., 1938, **18**, 161—162).— α -Phenylcinchonoyl chloride in ligroin and $Hg(CN)_2$ (6 hr. at the b.p.) yield α -phenylcinchononitrile, which when hydrolysed (cold dil. HCl) gives α -phenylcinchonic

acid, and is converted by Na in $C_5H_{11}OH$ into 2-phenyl-1:2:3:4-tetrahydrocinchonic acid.

R. T.

Degradation of quaternary ammonium salts of strychnine alkaloids. O. ACHMATOWICZ (Congr. int. Quim. pura apl., 1934, **9**, IV, 230—232; Chem. Zentr., 1936, ii, 2728; cf. A., 1934, 788).—Following the suggestion (A., 1932, 527) that strychnine and brucine contain the group $N \cdot CH_2 \cdot C(\cdot CH) \cdot CH$, exhaustive methylation of dihydrostrychnidine A (I) and dihydrobrucidine (II) has been effected. The following new bases were obtained from (I): $C_{20}H_{30}O_2N_2$, m.p. 159° (the OH-compound corresponding with methoxymethyltetrahydrostrychnine, which is obtained on methylating with Me_2SO_4) [O-Ac derivative, m.p. 254°, decomp. by heating into (I) and MeOAc]; $C_{21}H_{28}ON_2$, m.p. 142°, 196°. The last two de-bases contain C:C and NMe as they are degraded by H_2 and Pd-C (cf. A., 1933, 406). Methylstrychnidinium chloride gives a de-base, $C_{21}H_{27}ON(NMe)$, m.p. 176°, and methylbrucinium and methylstrychninium chlorides are degraded similarly, the latter to two bases, $C_{21}H_{23}O_2N(NMe)$, m.p. 145°, and $C_{21}H_{25}O_2N(NMe)$, m.p. 201°, both yielding the above base, m.p. 176°, on electrolytic reduction, as does the base of m.p. 142° on catalytic reduction. Dihydrobrucidine behaves analogously. Structural formulæ are advanced. A. H. C.

Strychnos alkaloids. XCIX. Hydrogenation of aponucidine and its derivatives. H. LEUCHS (Ber., 1938, **71**, [B], 1525—1528).—*apo*Nucidine (I) is hydrogenated (Adams) and then acetylated to N-acetyldihydroaponucidine [*perchlorate*, m.p. about 260° (decomp.) after blackening]. N-Acetylaponucidine [*perchlorate*, m.p. about 262° (decomp.), $[\alpha]_D^{25} -64^\circ$ in H_2O] is transformed by the successive action of Me_2SO_4 in C_6H_6 and 0.5N- $HClO_4$ into N-acetylaponucidine methoperchlorate, m.p. 240—245°, $[\alpha]_D^{25} -46^\circ$ in H_2O ; this is hydrogenated (PtO_2) and separated by $NH_2 \cdot CHCl_3$ into a compound which gives a methiodide, $C_{18}H_{30}O_2N_2, MeI$, m.p. 295—298° (decomp.), and a substance, $C_{17}H_{26}O_2N_2$ (methoperchlorate, m.p. 215—220°, decomp. about 260°). (I), Bz_2O , and NaOBz at 95—115° afford N-benzoylaponucidine, m.p. about 160°, decomp. 230—240°, $[\alpha]_D^{25} -49.2^\circ$ in H_2O , which gives analogously N-benzoylaponucidine methoperchlorate, m.p. about 247° (decomp.) after softening at 210°, $[\alpha]_D^{25} -13^\circ$ in H_2O . N-Methylaponucidine methiodide, m.p. about 302° (vac.; decomp.), is hydrogenated (PtO_2) to the compound, $C_{16}H_{26}ON_2, MeI, HI$, m.p. 312—317° (vac.; decomp.). N-Methylaponucidine dimethoperchlorate, m.p. >300°, is hydrogenated (PtO_2) to the compound, $C_{16}H_{26}ON_2, 2MeClO_4$, m.p. 280—282° (vac.; decomp.). H. W.

Synthesis of apomorphine dimethyl ether. J. M. GULLAND (Chem. and Ind., 1938, 774).—Examination of the papers of Avenarius and Pschorr (Ber., 1929, **62**, 321) and of Gulland *et al.* (J.C.S., 1929, 1791) shows that unequivocal statements attributing a synthesis of apomorphine Me_2 ether to the former authors are unjustified. H. W.

Menisine, isomeric with tetrandrine. T. Q. CHOU (Chinese J. Physiol., 1938, **13**, 167—171; cf.

A., 1935, 1433).—The methochloride of menisine (I) or tetrandrine (II) with boiling aq. 10% NaOH affords a product from which C_6H_6 extracts an optically inactive methine base, $C_{40}H_{46}O_6N_2$, m.p. 171° (methiodide, m.p. 257°), and a methiodide, m.p. 217°; the C_6H_6 -insol. portion gives a base, $C_{42}H_{54}O_{11}N_2$, m.p. 248° (decomp.), $[\alpha]_D^{25} +625^\circ$ in MeOH [methiodide, m.p. 258° (decomp.)]. The above methiodides when converted into methochlorides and boiled with aq. 10% NaOH afford NMe_3 and a substance, $C_{36}H_{32}O_6$, m.p. 221°. (I) at 150° in 3 hr. affords (II) completely.

J. L. D.

New aromatic arsenical derivatives. II. Acids and arsenical derivatives of benzophenone. E. V. ZAPPI and J. F. SALBELLAS (Anal. Assoc. Quim. Argentina, 1938, 26, 21—29; cf. A., 1937, II, 172).—Diazotised $CO(C_6H_4 \cdot NH_2 \cdot p)_2$ by the usual method yields benzophenone-4 : 4'-diarsinic acid, blackens when heated (semicarbazone, infusible), also obtained by oxidation of $CH_2(C_6H_4 \cdot AsO_3H_2 \cdot p)_2$ with CrO_3 or $KMnO_4$; with NaH_2PO_2 in dil. H_2SO_4 it gives 4' : 4''-arsenobisdibenzophenone-4 : 4'-arsinic acid, no m.p., $CH_2(o-NO_2 \cdot C_6H_3 \cdot AsO_3H_2 \cdot p)_2$, which with alkaline $KMnO_4$ gives 2 : 2'-dinitrobenzophenone-4 : 4'-diarsinic acid, no m.p.

F. R. G.

Configuration of heterocyclic compounds. IX. Optical resolution of 8-chloro-10-phenylphenoxarsine-2-carboxylic acid. (Miss) M. S. LESSLIE (J.C.S., 1938, 1001—1003).—5-Chloro-2-p-tolylxyphenylarsinic acid, m.p. 199—200°, prepared from 4-chloro-2-aminophenyl p-tolyl ether, with conc. H_2SO_4 gives 8-chloro-2-methylphenoxarsinic acid, m.p. 289—291°, converted by $HCl-SO_2$ into 8 : 10-dichloro-2-methylphenoxarsine, m.p. 171—172°. This compound and $MgPhBr$ yield 8-chloro-10-phenyl-2-methylphenoxarsine, m.p. 75—76°, oxidised ($KMnO_4$) to dl-8-chloro-10-phenylphenoxarsine-2-carboxylic acid, m.p. 220—221°. This acid has been resolved through d- α -phenylethylamine l-, m.p. 236—237°, $[\alpha]_D^{20} -71.7^\circ$ in MeOH, and l- α -phenylethylamine d-8-chloro-10-phenylphenoxarsine-2-carboxylate, $[\alpha]_D^{20} +71.3^\circ$ in MeOH, into l-, m.p. 202—203°, $[\alpha]_D^{20} -68.7^\circ$ in $COMe_2$, and d-8-chloro-10-phenylphenoxarsine-2-carboxylic acid, m.p. 202—203°, $[\alpha]_D^{20} +69.0^\circ$ in $COMe_2$. The acid shows high optical stability.

F. R. S.

Organo-derivatives of arsenic, antimony, mercury, and gold.—See B., 1938, 982—983.

Dissociation of hydrogen ions from the sulphates of amino-phenylboric acids.—See A., 1938, I, 457.

Mercury derivatives of aromatic compounds with an unsaturated side-chain. R. PRESTER (Rec. trav. chim., 1938, 57, 811—818).—The data of Manchot (A., 1919, i, 145; 1920, i, 519, 720, 780, 905) are extended and, in part, corr. Saffrole (I) and $Hg(OAc)_2$ in H_2O give the oily additive compound, converted by aq. NaCl into the compound, (I), $HgCl \cdot OH$, new m.p. 140—141°, reconverted into (I) by 2N-HCl at 60°. Eugenol (II) gives the compound, (II), $HgR \cdot OH$ ($R = OAc$), m.p. 120.5—121.5°, converted into the basic compounds, in which $R = Cl$, m.p. 103—104°, Br , m.p. 125—126°, and I,

m.p. 136°. With 2 mols. of $Hg(OAc)_2$ (II) gives the additive compound 1 : 2 : 5 : 4-
(OH)(OMe) $C_6H_3(HgCl \cdot OH) \cdot CH_2 \cdot CH \cdot CH_2 \cdot HgCl \cdot OH$ [regenerates (II)], which at 100° loses H_2O , yielding the compound 1 : 2 : 5 : 4-

(OH)(OMe) $C_6H_2(HgCl) \cdot C_5H_5 \cdot HgCl \cdot OH$ [does not regenerate (II)]. Eugenol Me ether (III) and $Hg(OAc)_2$ give a poor yield of the compound, (III), $Hg(OH) \cdot OAc$, m.p. 69—70°, converted by NaCl into the basic chloride, m.p. 114—115°.

R. S. C.

Osmotic pressure, mol. wt., and stability of gliadin.—See A., 1938, I, 456.

Filling of micro-combustion tubes.—See A., 1938, I, 478.

Qualitative micro-method for the identification of alkyl groups united to oxygen or nitrogen. Micro-Zeisel method. I. M. FURTER (Helv. Chim. Acta, 1938, 21, 872—879).—The substance is heated with HI (d 1.7) in presence of Pt tetrahedra and the vapours are passed through a P suspension, $Na_2S_2O_3$, and $CdSO_4$ solution. After being dried by $CaCl_2$ they pass into a constricted tube containing a well-cooled suspension of 3 : 5-(NO_2) $C_6H_3 \cdot CO_2Ag$ in anhyd. Et_2O . When the action is over the tube is sealed at the constriction and heated at 100°. The alkyl group is identified by determination of the m.p. of the alkyl dinitrobenzoate thus produced supplemented by observations on its mol. compound with $\alpha-C_{10}H_7 \cdot NH_2$.

H. W.

Characterisation of the acetyl group in medicinal chemicals by the formation of "lanthanum-blue." A. D. DEL BOCA and A. REMEZZANA (An. Farm. Biochim., 1935, 6, 111—116; Chem. Zentr., 1936, ii, 2167).—The Ac group in a series of medicinals (heroin, aconitine, aspirin, tannigen, $NHPhAc$, exalgin, phenacetin, but not with salophen) is indicated by the La-blue reaction of the product obtained by distilling with dil. H_2SO_4 (often in presence of $FeCl_3$).

A. H. C.

Improved Kurt Meyer titration. S. R. COOPER and R. P. BARNES (Ind. Eng. Chem. [Anal.], 1938, 10, 379).—Diisobutylene is preferable to $\beta-C_{10}H_7 \cdot OH$ for absorbing the excess of Br in the indirect Kurt Meyer titration of CH_2Bz_2 . Abs. MeOH is preferable to EtOH as a solvent for the Br. The method detailed gives results agreeing to within 1% as against 7% for the original method. The mean val. obtained for the % of enol form in CH_2Bz_2 is 95.66.

L. S. T.

Sulphuric acid analysis of gaseous olefines. M. P. MATUSZAK (Ind. Eng. Chem. [Anal.], 1938, 10, 354—360).—Data indicating the influence of the following factors on the analytical results obtained in the determination of gaseous olefines by absorption in H_2SO_4 are given: reversibility of absorption; solubility of gaseous hydrocarbons in H_2SO_4 ; effect of acid-sol. absorption products on solubility of hydrocarbons; solubility of hydrocarbons in pptd. polymeric products and liberation of unabsorbed gas by strong adsorbents. Apparatus and technique to overcome these difficulties are described with a view of making the determination accurate for low and high concns. of gaseous olefines.

F. N. W.

Determination of small quantities of methyl bromide in air. R. L. BUSBEY and N. L. DRAKE (Ind. Eng. Chem., [Anal.], 1938, 10, 390—392).—The air containing MeBr is passed through 25 c.c. of a 2% EtOH-KOH solution at 68° for 1 hr. in a specially designed apparatus, the mixture diluted with 225 c.c. of H₂O, and the EtOH removed by distillation. To the residual liquid (150 c.c.) are added 20 c.c. of aq. NaOCl solution (7 g. Cl per 100 c.c. of 12% aq. NaOH), 5 g. of NaCl, and 10 g. of boric acid, and after heating (100°; 0.25 hr.), 20 c.c. of 10% aq. HCO₂Na solution are added to the mixture to destroy excess of HOCl. After boiling for 5 min. and cooling, solid KI, a few drops of 5% aq. NH₄ molybdate, and 50 c.c. of 2*N* aq. HCl are added and the liberated I is titrated with 0.1*N*-Na₂S₂O₃. The average error reported on analyses of 13 samples ranging from 0.048 to 0.0065 g. is -1.7%. F. N. W.

Determination of ethyl acetate. E. BUTSCHOWITZ and A. VLK (Ann. Chim. Analyt., 1938, [iii], 20, 175—177).—The EtOAc is weighed in a sealed bulb and saponified by KOH. A. LI.

Extension of the resorcinol-sulphuric acid reaction to the succinate ion. G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1936, 74, 12—17; Chem. Zentr., 1936, ii, 827).—0.02—0.04 g. of the acid, anhydride, or succinate is heated to boiling with 2 c.c. of H₂SO₄ and 4 drops of NaBr-NaOBr solution, Br is removed in an air stream, the solution is allowed to cool for 1 min., and 1 drop of the reagent (2 g. of resorcinol, 0.5 c.c. of H₂SO₄, H₂O to 100 c.c.) is added. A wine-red colour, with a characteristic absorption band at 5275 Å., results. H. J. E.

Möhler-Denigès reagent for tartaric acid. C. H. LIBERALLI (Rev. Quim. Farm., 1935, 1, 12—15; Chem. Zentr., 1936, ii, 2184).—MnO₄' or Cr₂O₇' in small quantity do not interfere with the resorcinol test for tartaric acid (I). Gluconic, lactic, and pyroracemic acids in presence of Br' or I', or citric acid in presence of Br', I', or MoO₄'', give colorations similar to that obtained with (I). A. J. E. W.

Determination of amino-acids. W. H. STEIN, C. NIEMANN, and M. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 1703—1704).—When NH₂-acids in H₂O are treated with precipitants, the amount remaining in solution is often quantitatively governed by the solubility product of the ppt. Some NH₂-acids can thus be determined by weighing the amount of ppt. produced by varying amounts (excess) of precipitant. Glycine, *l*-alanine, and *l*-leucine are thus determined with dioxypyridic acid, *l*-proline with rhodanilic acid, and tyrosine with dioxanilic acid. R. S. C.

Separation of the chrysanthemumcarboxylic acids. A. A. PANTSIOS (Ind. Eng. Chem., [Anal.], 1938, 10, 386—387).—As steam-distillation of chrysanthemum-monocarboxylic acid (I) causes decomp., acid methods of pyrethrin I analysis are inaccurate. It is possible to separate the two chrysanthemum acids by the selective extraction of (I) with light

petroleum, although the method is not sufficiently accurate for the analysis of pyrethrum flowers.

F. N. W.

Determination of pyridine. C. BELCOT (Ann. Chim. Analyt., [iii], 20, 173—175).—Small quantities of C₅H₅N are determined by pptg. with KCNS and CuSO₄, and determining excess of Cu iodometrically, but for large quantities the method of Schultze (A., 1888, 539) is sufficiently accurate. A. LI.

Fröhde's reagent: a reagent for morphine and for other phenolic compounds. C. C. FULTON (J. Lab. clin. Med., 1938, 53, 625—630).—Fröhde's reagent provides a sensitive and sp. test for morphine, the main colour sequence being intense purplish-red, changing to weak brown or even fading out completely, and then developing as strong bright green.

T. H. H.

Identification of ecgonine. F. AMELINK (Pharm. Weekblad, 1938, 75, 861—864).—Characteristic microcryst. ppts. are obtained with ecgonine solutions and PtCl₄-NaI, AuCl₃-NaBr, HgCl₂, and Dragendorff's reagent. The sensitivity in all cases is 0.1—0.2%. S. C.

Potentiometric and conductometric analysis of cinchonidine salt solutions. H. L. PEDERSEN (Dansk Tidsskr. Farm., 1938, 12, 161—187).—0.01*N*-Cinchonidine salts may be titrated potentiometrically in excess of HCl against 0.1*N*-NaOH with an accuracy of 0.25%. The *p*_H of cinchonidine dihydrochloride (I) solutions has been measured over the range 0.02—0.005*N*. The titration of cinchonidine tetrasulphate has been investigated. Conductometric titration of 0.01*N*-(I) against *N*-NaOH gives vals. 2% > against *N*-AgNO₃. The solubilities of (I) and cinchonidine disulphate have been measured conductometrically.

M. H. M. A.

Identification of alkaloids. K. E. JACKSON (Ind. Eng. Chem., [Anal.], 1938, 10, 380—381).—A systematic summary of known methods for the identification of 42 common alkaloids. F. N. W.

Determination of alkaloids by a combined precipitation-acidimetric process. R. DIETZEL and W. PAUL (Süddeuts. Apoth.-Ztg., 1936, 76, 474—477; Chem. Zentr., 1936, ii, 1577).—50—100 mg. of base are dissolved in 15 c.c. of 0.1*N*-HCl, mixed slowly with 30 c.c. of a solution of 1 g. of I and 1.5 g. of KI in 100 c.c. of H₂O, made up to 50 c.c., and shaken for 5 min. The solution is filtered, decolorised with Na₂S₂O₃, and the amount of acid fixed as X.HI.I_x (X = base) determined by titrating HCl remaining in the filtrate against 0.1*N*-alkali using phenolphthalein. K₂HgI₄ may replace KI₃. The procedure is valid for morphine, atropine, strychnine, brucine, narcotine, papaverine, cocaine, hyoscyamine, veratrine, codeine, aconitine, and for colchicine on flocculating the complex with NaCl but not for nicotinic, quinine, piperine, berberine, apomorphine, or purines. A. H. C.

Determination of mercury in inorganic and organic compounds and pharmaceutical preparations.—See A., 1938, I, 473.

A., II.—Organic Chemistry

OCTOBER, 1938.

Chemical homology. J. K. SENIOR (J. Org. Chem., 1938, 3, 1—10).—A discussion. Previous definitions of homology are unsatisfactory because of the attempt to limit the term only to useful and instructive cases. A general definition is proposed together with modifications which enable types of homology to be classified and any particular type to be designated. Suitable nomenclature is suggested. Illustrations of the system are given. H. G. M.

Large molecules in synthetic organic chemistry. G. O. CURME (J. Franklin Inst., 1938, 226, 187—202).—A general account. K. W. P.

Detection of radicals in the chemical decomposition of alkyl iodides. R. VAN TASSEL (Natuurwetensch. Tijds., 1938, 20, 83—85).— C_2H_4 polymerises at 300° in presence of EtI and Hg vapour. The rate of polymerisation \propto the concns. of C_2H_4 and EtI. S. C.

Reaction of oxygen atoms with methane. E. W. R. STEACIE and N. A. D. PARLEE (Canad. J. Res., 1938, 16, B, 203—209).—O atoms (produced by a discharge-tube method) and CH_4 at 37—330° give CO and a smaller amount of CO_2 , but no C_2H_6 or higher hydrocarbons. The activation energy is 8 kg.-cal. The reaction is thus: $O + CH_4 \rightarrow H_2O + CH_3$; $CH_2 + O \rightarrow CH_2O$; $CH_2 + 2O \rightarrow HCO_2H$; $CH_2O + O \rightarrow CO + H_2O$; $HCO_2H + O \rightarrow CO_2 + H_2O$. Formation of CH_3 must be slower than the oxidation of CH_2O and HCO_2H , as these products were not isolated. The reaction, $CH_2 + CH_4 \rightarrow C_2H_6$, must have an activation energy >11—12 kg.-cal. R. S. C.

Optically active aliphatic hydrocarbons. D. DUVEEN and J. KENYON (Bull. Soc. chim., 1938, [v], 5, 1120—1126).—*dl-n*-Propylsec.-butylcarbinol, b.p. 70°/15 mm., obtained in 62% yield from $MgBu^sCl$ and Pr^aCHO , is transformed by $o-C_6H_4(CO)_2O$ in C_5H_5N at 60—70° into *dl-n*-propylsec.-butyl *H* phthalate, m.p. 52°. This is resolved by brucine in $COMe_2$ into (+)-*n*-propylsec.-butylcarbinyl *H* phthalate, m.p. 55°, $[\alpha]_{5461}^{20} +17.13^\circ$ in C_5H_5N , $+15.8^\circ$ in $CHCl_3$, $+19.9^\circ$ in CS_2 (other vals. recorded) [brucine salt (I), m.p. 159° (decomp.)], hydrolysed (KOH) to (+)-*n*-propylsec.-butylcarbinol, b.p. 70°/16 mm., $[\alpha]_{5461}^{20} +10.60^\circ$. Treatment of the alcohol with I and red P followed by Zn—Cu in Et_2O yields (+)- γ -methylheptane, b.p. 118°, $[\alpha]_{5461}^{20} +0.72^\circ$, which thus has been very extensively racemised during the final changes. Treatment of the mother-liquors from (I) by strychnine leads to (—)-*n*-propylsec.-butylcarbinyl *H* phthalate, m.p. 51—52°, $[\alpha]_{5461}^{20} -17.2^\circ$ in $CHCl_3$ (strychnine salt), whence (—)-*n*-propylsec.-butylcarbinol, b.p. 70°/16 mm., $[\alpha]_{5461}^{20} -5.23^\circ$. *dl*-Ethylsec.-butylcarbinol,

b.p. 58—60°/15 mm., obtained in 65% yield from $MgBu^sCl$ and $EtCHO$, yields isomeric ethylsec.-butylcarbinyl *H* phthalates, m.p. 94—96° and 81—82°, respectively. The latter gives cryst. salts with brucine, strychnine, and quinidine by means of which it could not be resolved. The former is resolved by brucine in $COMe_2$ into (+)-ethylsec.-butylcarbinyl *H* phthalate, m.p. 91—92°, $[\alpha]_{5461}^{20} -3.30^\circ$ in CS_2 (brucine salt, m.p. 161—162°), and (—)-ethylsec.-butylcarbinyl *H* phthalate, m.p. 91—93°, $[\alpha]_{5461}^{20} -3.6^\circ$. Resolution is effected more slowly through the quinidine salt. (—)-Ethylsec.-butylcarbinol, b.p. 51°/14 mm., $[\alpha]_{5461}^{20} -0.67^\circ$, is transformed by $SOCl_2$ in light petroleum into δ -chloro- γ -methylhexane, b.p. 37°/15 mm., $[\alpha]_{5893}^{20} -1.19^\circ$. II. W.

Addition of hydrogen fluoride to the double linking. A. V. GROSSE and C. B. LINN (J. Org. Chem., 1938, 3, 26—32).— C_2H_4 when autoclaved with anhyd. HF at temp. between 0° and 90° and pressures between 10 and 20—25 atm. (depending on the temp.) gives EtF. The yield, based on the C_2H_4 reacting, increases at higher temp., and is >80% at 90° and 0% at -60°. By similar methods $CHMe:CH_2$ gives Pr^sF , in accord with Markovnikov's rule, and cyclohexene gives cyclohexyl fluoride, the yields diminishing with increasing temp. and prolongation of reaction time. The reaction is not catalytic and takes place as readily in paraffin as in metal vessels. Addition of 0.004—0.03 mol. of BF_3 per mol. of HF has no beneficial effect. In all cases polymerisation products were formed. cycloPropane at 25° gives Pr^sF and a little Pr^tF . No reaction takes place between $CHMe:CH_2$ and 50% aq. HF at 25° during 18 hr. H. G. M.

Peroxide effect in the addition of reagents to unsaturated compounds. XIX. Addition of hydrogen bromide to trichloroethylene. M. S. KHARASCH, J. A. NORTON, and F. R. MAYO (J. Org. Chem., 1938, 3, 48—54).—In presence of small amounts of $AlCl_3$ and of $FeCl_3$, HBr adds to $CHCl:CCl_2$ (I) giving $\alpha\beta$ -trichloro- α -bromoethane, b.p. 152°/760 mm., from which (I) is recovered by means of Zn in hot EtOH, or NaOPh—EtOH. No addition occurs in presence of antioxidants even after prolonged illumination. No addition of HI to (I) took place in an equimol. mixture in the dark or when illuminated, some $CHCl_2\cdot CH_2Cl$ and I being formed in the latter case. In presence of air and peroxides HBr adds to (I) giving $CHCl_2\cdot CHClBr$, the reaction being accelerated by light. H. G. M.

(A) Laboratory furnace and experimental equipment for, and (B) performance of the catalyst used in, the preparation of divinyl from

alcohol. (C) Alcohols of the series C_5 and C_6 , (D) aldehydes and ketones, and (E) piperylene and amylene in the products of catalytic decomposition of alcohols by the S. V. Lebedev method. (F) Utilisation of ψ -butylene obtained in divinyl synthesis from alcohol. S. V. LEBEDEV [with N. Z. ANDREEV, J. A. GORIN, I. K. GORN, S. G. KIBIRSKITS, G. G. KOBLJANSKI, A. M. KOGAN, A. V. KOZLOVSKAJA, V. P. KRAUSE, M. A. KRUPUISHEV, I. A. LIVSCHITZ, O. M. NEIMARK, G. N. SIBIRJAKOVA, J. M. SLOBODIN, and I. A. VOLSHINSKI] (Trud. Gosud. Op. Zav. Sintet. Kautschuka, 1934, B, III, 7—16, 16—40, 41—44, 44—45, 50—68, 68—85).—(A) Laboratory and micro- (capacity 5 c.c. of EtOH) -furnaces and a furnace with reaction chambers of 1 m. length are described. EtOH is preheated to 400—525°, passed over the catalyst, the products are cooled, and uncondensed gases absorbed (e.g., in turpentine). $(CH_2:CH)_2$ and ψ - C_4H_8 are recovered by fractionating the solution and removing MeCHO by passing through 50% aq. NaOH.

(B) The catalyst (composition not given), which is preferably of worm-like shape (diameter 1—3 mm.) and not compressed, consists of a dehydrogenating and a dehydrating substance (cf. B., 1930, 939). The furnace is of Cu or enamelled or Al-plated Fe; chambers of length 1 m. and 3 m. are compared. The unfavourable effect of Et_2O and H_2O , and the slightly favourable effect of 5—7% of MeCHO, are noted. Spent catalyst, which causes increase in the H_2 , MeCHO, and BuOH yields, is regenerated by admitting air into the catalyst chamber.

(C) Normal primary saturated alcohols (C_{5-6}) are obtained.

(D) CO_2 , MeCHO, but-, croton-, valer-, hex-, and oct-aldehydes are obtained.

(E) The condensate from the prep. and the residues from the rectification of $(CH_2:CH)_2$ are rectified, the fractions of b.p. 30—45° isolated and united, and fractions of b.p. 35—37° and 37—40° collected. The diene and olefine (in each fraction) are brominated, the bromides separated, and piperylene and amylene regenerated. Condensation reactions are also described.

(F) ψ - C_4H_8 obtained as a by-product in the prep. of synthetic rubber from $(CH_2:CH)_2$ is treated in the liquid phase with 72—75% H_2SO_4 to yield 83% of Bu^oOH and thence (with Ac_2O and fused NaOAc) Bu^oOAc. $(CH_2:CH)_2$ in ψ - C_4H_8 could be removed by Na but not by H_2SO_4 . The use of Cu or Pb apparatus is recommended. CH. ABS. (c)

Acetylene and sulphuric acid. J. MILBAUER (Arh. Hemiju, 1938, 12, 73—83).—Pure C_2H_2 reacts with conc. H_2SO_4 , which is thereby coloured brown. The reaction is catalysed by $HgSO_4$, SeO_2 , V_2O_5 , Ag_2SO_4 , and MoO_3 , but not $CuSO_4$, and is retarded by $(NH_4)_2SO_4$. R. T.

Alkylacetylenes and their addition products. XXVI. Halogenation of Δ^a -hexinene in methanol. J. J. VERBANC and G. F. HENNION. XXVII. Reactions of dialkoxyalkanes with alkenylmagnesium bromides. A. L. KRANZFELDER and R. R. VOGT. XXVIII. Reactions of dialkylacetylenes. E. A. BRIED and G. F. HENNION (J.

Amer. Chem. Soc., 1938, 60, 1711—1713, 1714—1716, 1717—1719; cf. A., 1938, II, 167).—XXVI. Cl_2 with $CH_3C\equiv Bu^a$ in MeOH leads to addition of Cl_2 and MeOH. At 0—5° 20% of $\alpha\beta$ -dichloro- Δ^a -hexene (I), b.p. 60—61°/34 mm., and 24% of $\alpha\alpha$ -dichloro- $\beta\beta$ -dimethoxyhexane (II), b.p. 76—78°/2 mm., are formed by way of α -chloro- β -methoxy- Δ^a -hexene (III). At 25—30° 18% of (I), 35% of (II), and 37% of $\alpha\alpha$ -dichlorohexan- β -one (IV), b.p. 64—66°/10 mm., are obtained. The (IV) arises by addition of Cl_2 to (III) and subsequent loss of MeCl (identified); its structure is proved by conversion by $Ca(OCl)_2$ into $CHCl_3$ and Bu^aCO_2H . In CCl_4 only (I) (25% yield) and a polymeride are obtained. Br in MeOH gives 92.5% of $\alpha\beta$ -dibromo- Δ^a -hexene, b.p. 89—91°/30 mm. $CCl_3C\equiv Bu^a$ and Cl_2 in MeOH give 83% of α -chloro- $\beta\beta$ -dimethoxyhexane, b.p. 77—80°/14 mm., converted by p - $C_6H_4Me\cdot SO_3H$ into (III) (92.5% yield), b.p. 90—91°/65 mm., which with Cl_2 in MeOH at 25—30° gives 60% of (II) and with p - $C_6H_4Me\cdot SO_3H$ in aq. MeOH gives 82% of α -chlorohexan- β -one, b.p. 73—74°/20 mm. MeOCl is not concerned in these reactions, for which an electronic mechanism is suggested.

XXVII. $CHR(OR')_2$ with $C\equiv Bu^a:C\cdot MgBr$ gives, by elimination of $MgBr\cdot OR'$, α -ethoxy-, b.p. 90°/24 mm., and α -propoxy- Δ^b -heptinene, b.p. 61°/4 mm., γ -ethoxy- Δ^b -noninene (V), b.p. 105°/25 mm., and α -ethoxy- α -phenyl- Δ^b -heptinene (VI), b.p. 115°/4 mm. $C_5H_{11}\cdot C\equiv C\cdot MgBr$ and $CHMe(OEt)_2$ give β -methoxy- Δ^v -noninene, b.p. 108°/40 mm. Similarly, $C\equiv Bu^a:C\cdot CHEt\cdot OEt$ and $C\equiv Bu^a:C\cdot MgBr$ give η -ethoxy- Δ^{e6} -tridecadi-inene, b.p. 121°/4 mm., whereas $C\equiv Bu^a:C\cdot CH(OMe)_2$ gives η -methoxy- η -methyl- Δ^e -undecene, b.p. 83°/4 mm. $CHMe(OEt)_2$ with $CH_3C\equiv MgBr$ and $(iC\equiv MgBr)_2$ gives $CH_3C\equiv CHMe\cdot OEt$ and $(iC\equiv CHMe\cdot OEt)_2$, respectively. $CHPh(OEt)_2$ and $CH_3C\equiv MgBr$ give $CH_3C\equiv CHPh\cdot OEt$. $CH_2(OPr)_2$ and $(iC\equiv MgBr)_2$ give $(iC\equiv CH_2\cdot OPr)_2$. The yields vary greatly according to the acetal used. The prep. of $CHEt(OEt)_2$, b.p. 122—123°, and $CHMe(OEt)_2$ is modified. Addition of EtOH to $CH_3C\equiv Bu^a$ and $HgO\cdot BF_3$ gives $\alpha\alpha$ -diethoxy- Δ^b -heptinene, b.p. 97—98°/10 mm. $C_5H_{11}\cdot C\equiv CNa$ (prep. by $NaNH_2$ in liquid NH_3) and $CHMe(OEt)_2$ give β -ethoxy- Δ^v -noninene, b.p. 108°/40 mm. $C\equiv Bu^a:C\cdot CH(OEt)_2$ with $MgEtBr$ and $MgPhBr$ gives (V) and (VI), respectively, which proves the structure of the products.

XXVIII. Good yields of dialkylacetylenes are obtained from $CH_3C\equiv Na$, $NaNH_2$, and RCl in liquid NH_3 only if R has a moderate mol. wt. The yield of Δ^a -octadecene, b.p. 163—164°/7 mm., is increased from 15 to 27% by 8 atm. pressure. Δ^v -Tetradecene, b.p. 124°/15 mm., is prepared in 38% yield. $C_{10}H_{21}Br$ gives $CH_3C\equiv C_{10}H_{21}$ and $C_{10}H_{21}\cdot NH_2$. $(iC\equiv Bu^a)_2$ with H_2 -Raney Ni at 3.7—1.3 atm. gives n - $C_{10}H_{22}$, with $Br\cdot CHCl_3$ gives dibromide fractions, b.p. 123—124°/17 mm. and 127—128°/17 mm., with Pr^oOH (Hg catalyst) at 80° gives decan- ϵ -one, b.p. 106—108°/27 mm., with $MeOH\cdot HgO\cdot BF_3\cdot CCl_3\cdot CO_2H$ gives impure $\epsilon\epsilon$ -dimethoxydecane, b.p. 98—99°/10 mm., with $AcOH$ (Hg catalyst) gives ϵ -acetoxycyclopentene, b.p. 95—97°/10 mm., and with $(CH_2\cdot OH)_2$ (Hg catalyst) gives 2-butyl-2- n -amyl-1:3-dioxacyclopentane [*dioxolane*], b.p. 103—105°/10 mm. $(CNS)_2$ in C_6H_6 with $(iC\equiv Ph)_2$ gives a cryst., m.p. 192—

193°, and with $(\text{C}_6\text{H}_{17})_2$ an amorphous product, but $(\text{CBu}^a)_2$ does not react. R. S. C.

Pinacols of pinacolin. H. J. BACKER (Rec. trav. chim., 1938, 57, 967—988; cf. Delacre, A., 1907, i, 579).— $(\text{Bu}^v\text{CO})_2$ with MgMeI in Et_2O , followed by hydrolysis, gives only $\beta\gamma\epsilon\epsilon$ -pentamethylhexan- γ -ol-8-one, m.p. 60°, but with excess of MgMeI in PhMe yields a *pinacol* (I) of pinacolin, m.p. 69°. Reduction of pinacolin with $\text{Na} + \text{H}_2\text{O}$ in Et_2O yields a solid, m.p. 73.5—74.5°, which with HCl gives an isomeric *pinacol* (II), m.p. 88°. Measurements of the rates of oxidation (to pinacolin) by $\text{Pb}(\text{OAc})_4$ in AcOH , and by $(\text{EtCO}_2)_4\text{Pb}$ in PrOH , and of the m.p. of mixtures of (I) and (II) show that the solid, m.p. 74.5°, is a mixture of (I) and (II) in the ratio 2 : 3. (II) is more stable to HCl than (I), but both (I) and (II) with dil. H_2SO_4 give pinacolin, $\text{CMe}_2\text{:CMe}_2$, and $\beta\gamma$ -ditert-butylbutadiene [also obtained by the action of PCl_3 on (I) or (II)] (identified as the dibromide). With $p\text{-NO}_2\text{:C}_6\text{H}_4\text{:CHO}$ and HCl , (I) gives an *acetal*, m.p. 139—140°, but (II) does not react. It is concluded that (I) is the *dl*- and (II) the *meso*-form, the difference in properties being due to the large Bu^v groups. A by-product in the reduction of pinacolin is $\text{CMeBu}^v\text{:CH:COBu}^v$, identified by reduction $[\text{Al}(\text{OPr}^i)_3]$, dehydration, and treatment with SO_2 in Et_2O , giving the sulphone of $\text{CHBu}^v\text{:CH:CBu}^v\text{:CH}_2$.

A. Li.

Determination of the degree of unsaturation of the higher alcohols. V. G. SCHAPOSCHNIKOV and N. A. KALINITSHEVA (Trud. Gosud. Op. Zav. Sintet. Kautschuka, 1934, B, III, 110—117).—Analyses were carried out by hydrogenation, with Pt and Ni catalysts, and by the Rosenmund Br titrimetric method (cf. A., 1923, ii, 886; B., 1924, 23).

CH. Abs. (e)

Isolation of the intermediate product in the catalytic isomerisation of dipropenyl glycol. L. MARTINEAU and J. WIEMANN (Compt. rend., 1938, 207, 243—245).—Dipropenyl glycol at 130° in presence of Cu deposited on Th affords dibutyl (I) (50% yield), b.p. 65°/17 mm. At 110°, besides (I), ϵ -hydroxy- δ -keto- Δ^4 -octadiene (II), b.p. 91°/13 mm. (30—40% yield), is formed. The Raman spectrum of (II) shows lines due to two double linkings, one propenyl, the other terminal.

J. L. D.

Fission of $\beta\epsilon$ -dimethyl- Δ^v -hexine- $\beta\epsilon$ -diol. A. T. BABAJAN (J. Gen. Chem. Russ., 1938, 8, 578—580).— $(\text{OH}\cdot\text{CMe}_2\cdot\text{C})_2$ yields $\text{OH}\cdot\text{CMe}_2\cdot\text{C:CH}$ and COMe_2 when distilled from CaC_2 , C_2H_2 and COMe_2 when distilled from K , and COMe_2 and H_2O when heated with CaCO_3 .

R. T.

Condensation products of glycerol and halogeno- and hydroxy-ketones. V. V. EVLAMPIEV and V. M. ZOROASTROVA (Utschen. Zap. Univ. Kazan, 1937, 97, No. 8, 71—82).—By shaking glycerol with $\text{COMe}\cdot\text{CH}_2\text{X}$ in presence of HCl and Na_2SO_4 or ZnCl_2 the following cycloacetals,

$\text{OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{O}$
 $\text{CH}_2\cdot\text{O} > \text{CMe}\cdot\text{CH}_2\text{X}$, were prepared: $\text{X} = \text{Cl}$, b.p. 127—129°/14—15 mm.; $\text{X} = \text{Br}$, b.p. 134—135°/14—15 mm.; $\text{X} = \text{I}$, b.p. 139—141°/13 mm. (decomp.); $\text{X} = \text{OAc}$, b.p. 148—149°/11 mm.; with N^* (A., II.)

aq. $\text{Ca}(\text{OH})_2$ it forms the compound $\text{X} = \text{OH}$, b.p. 153—154°/13 mm. J. J. B.

Compounds of bivalent carbon. H. SCHEIBLER (Congr. int. Quim. pura apl., 1934, 9, IV, 250—254; Chem. Zentr., 1936, ii, 2695).—Compounds (e.g., Na hydroxyethoxymethylene; cf. A., 1934, 390) and $\text{C}^{\text{II}}(\text{OR})_2$ (e.g., the acetals of CO ; cf. A., 1936, 312; 67; 1933, 491) must contain C^{II} . A. H. C.

Rearrangement of vinyl allyl ethers. C. D. HURD and M. A. POLLACK (J. Amer. Chem. Soc., 1938, 60, 1905—1911).—The change, $\text{CH}_2\text{:CR}\cdot\text{O}\cdot\text{CH}_2\text{:CH:CH}_2 \rightarrow \text{CH}_2\text{:CH}\cdot[\text{CH}_2]_2\cdot\text{CRO}$, by pyrolysis, analogous to the arrangement of Ph allyl ethers, is realised. Vinyl allyl ether (I), b.p. 65—65.2°/733 mm., is best (51%) obtained from β -bromoethyl allyl ether (II), b.p. 68.5—69°/36 mm., and powdered KOH at 110—174°; a 12—19% yield is obtained from $\alpha\alpha$ -diallyloxyethane (III), b.p. 148—149°/753 mm., and P_2O_5 in NPhMe_2 or quinoline, and a trace by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$; a trace is obtained by the action of Zn dust (not Na) at 148° on $\beta\beta$ -diallyloxyethyl bromide, b.p. 102—104°/23 mm. [prep. in 26.4% yield from $\text{CH}_2\text{Br}\cdot\text{CHO}$, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$ (IV), and a little H_2SO_4]. 62—68% of (III) is obtained from MeCHO , (IV), and CaCl_2 at 0°. $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{ONa}$ and $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Br}$ at 100° give 77—81% of β -hydroxyethyl allyl ether, b.p. 63—64°/18—19 mm., which with PBr_3 in $\text{EtOH}\text{-C}_5\text{H}_5\text{N}$ gives 45% of (II). $\text{CH}(\text{OEt})_3$, COMe_2 , and a little $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ in hot, abs. EtOH give 75% of $\beta\beta$ -diethoxypropane, b.p. 113—115°, which with (IV) and a little $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ gives 38% of $\beta\beta$ -diallyloxy- (V), b.p. 61°/26 mm., and 12% of β -ethoxy- β -allyl-propane (VI), b.p. 43—45°/26 mm. When heated with a little $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$, (V) gives allyl isopropenyl ether (VII), b.p. 87.5—88°/745 mm., also obtained similarly in poor yield from (VI). $\text{CH}_2\text{Br}\cdot\text{CHO}$, $(\text{CH}_2\text{Br}\cdot\text{CHO})_3$, (IV), and HCl at 0° give 62% of α -chloro- β -bromoethyl allyl ether, which with MgPhBr in Et_2O at 0° gives β -bromo- α -phenylethyl allyl ether, b.p. 129—130°/12 mm. (with some Ph_2), converted by distillation with powdered KOH into α -phenylvinyl allyl ether [α -allyloxystyrene] (VIII) (25% yield), b.p. 104—105°/12 mm. With $\text{HCl}\text{-EtOH}$ (I), (VII), and (VIII) give readily MeCHO , COMe_2 , and COPhMe , respectively. In boiling Ph_2O (252—255°; not at 215—218°) (I) gives 50% of Δ^v -pentenal, b.p. 103—104°/749 mm. (dimedone compound, m.p. 98°), identified by conversion by $\text{O}_3\text{-Ag}_2\text{O}$ into HCO_2H and $\text{CO}_2\text{H}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$. (VII) gives $\text{CH}_2\text{:CH}\cdot[\text{CH}_2]_2\cdot\text{COMe}$ quantitatively at 255°, and some change occurs at 200°. (VIII) gives $\text{CH}_2\text{:CH}\cdot[\text{CH}_2]_2\cdot\text{COPh}$ readily at the b.p./760 mm., and some change occurs at 175°. The effect of α -substituents in the vinyl group is thus marked.

R. S. C.

Conjugated systems. VII. Synthesis and properties of $\beta\gamma$ -halide ethers from butadiene. A. A. PETROV (J. Gen. Chem. Russ., 1938, 8, 487—497).— $(\text{CH}_2\text{:CH})_2$ in a no. of alcohols and $\text{PhSO}_2\cdot\text{NBr}_2$ were shaken at -12° ; the resulting ethers extracted with Et_2O and treated with Cl_2 or Br in CHCl_3 yielded the ethers $\text{CH}_2\text{Br}\cdot\text{CH}(\text{OR})\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$ ($\text{R} = \text{Me}$, b.p. 97—97.5°/10 mm.; $\text{R} = \text{Et}$, b.p. 104—104.5°/10 mm.; $\text{R} = \text{Bu}^a$, b.p. 130°/10 mm.; $\text{R} = \text{CH}_2\text{Bu}^b$, b.p.

134—135°/10 mm.) or $\text{CH}_2\text{Br}\cdot\text{CH}(\text{OR})\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ ($\text{R} = \text{H}$, b.p. 141—141.5°/10 mm.; $\text{R} = \text{Me}$, b.p. 120.5°/10 mm.; $\text{R} = \text{Et}$, b.p. 127°/10 mm.; $\text{R} = \text{Pr}^a$, b.p. 137°/10 mm.; $\text{R} = \text{Bu}^a$, b.p. 146—146.5°/10 mm.; $\text{R} = \text{Bu}^b$, b.p. 143.5—145°/10 mm.; $\text{R} = \text{CH}_2\text{Bu}^b$, b.p. 154.5°/10 mm.). The ethers were boiled with KOH in EtOH in presence of quinol, to yield the ethers $\text{CH}_2\text{C}(\text{OR})\cdot\text{CX}\cdot\text{CH}_2$ ($\text{R} = \text{Me}$, $\text{X} = \text{Cl}$, b.p. 64—67°/103 mm., $\text{X} = \text{Br}$, b.p. 48.5—49.5°/24 mm.; $\text{R} = \text{Et}$, $\text{X} = \text{Cl}$, b.p. 75—77°/86 mm., $\text{X} = \text{Br}$, b.p. 63.5—64°/24 mm.; $\text{R} = \text{Bu}^a$, $\text{X} = \text{Cl}$, b.p. 66.5—67°/12 mm.; $\text{R} = \text{Bu}^b$, $\text{X} = \text{Br}$, b.p. 65.5—66°/10 mm.; $\text{R} = \text{CH}_2\text{Bu}^b$, $\text{X} = \text{Cl}$, b.p. 76.5—77°; $\text{X} = \text{Br}$, b.p. 87.5°/12 mm.). These ethers readily polymerise, to yield resinous and rubber-like products, and are converted by dil. aq. H_2SO_4 into γ -chloro-, b.p. 38.5°/30 mm., or γ -bromo- Δ^7 -buten- β -one, b.p. 38.5—39°/12 mm. R. T.

Benzylisothiocarbamide and its application to the identification of organic acids. S. VEIBEL and H. LILLELUND (Bull. Soc. chim., 1938, [v], 5, 1153—1158).—Benzylisothiocarbamide hydrochloride, (I), obtained in 92% yield from $\text{CS}(\text{NH}_2)_2$ and CH_2PhCl in boiling EtOH- H_2O , exists in two polymorphous modifications, m.p. 150—151° and 175—176°, respectively. Identical salts are obtained from each variety. For identification the acid is dissolved in 10 c.c. or the requisite amount of H_2O and the solution is neutralised to methyl-red with NaOH and then made slightly acid with HCl. The solution of (I) in H_2O is added and the mixture is kept at 0° until crystallisation is complete. It is crystallised from EtOH or EtOH- H_2O . The following normal salts of benzylisothiocarbamide are described: *formate*, m.p. 150—151°; *acetate* (+ H_2O), m.p. 135—136°; *propionate*, m.p. 151—152°; *glycollate*, m.p. 146—147°; *oxalate*, decomp. 195—196° when slowly heated, 203° when placed in bath preheated at 198°; *ethylmalonate* (+ $2\text{H}_2\text{O}$), m.p. 120—121°; *fumarate* (+ H_2O), decomp. 182—183°; *benzene-o-disulphonate*, decomp. 205—206°. The following *H* salts are described: *malonate*, decomp. 145—146°; *maleate*, decomp. 173—174°; *benzoate*, m.p. 166.5—167.5°; *cinnamate*, m.p. 178—179°; *o-bromobenzoate*, m.p. 170—171°; *salicylate*, m.p. 147—148°; *anisate*, m.p. 184—185°; *anthranilate*, m.p. 142—143°; *amygdalate*, m.p. 164—165°; *benzenesulphonate*, m.p. 148—149°; *o-*, m.p. 170—171°; and *p-*, m.p. 182—183°; *-toluenesulphonate*; *sulphosalicylate* (1:2:3), m.p. 203—204°; *sulphanilate*, m.p. 187—188°; *benzene-m-disulphonate*, m.p. 163—164°. H. W.

Kinetics of the reaction between benzyl chloride and formic acid.—See A., 1938, I, 463.

Stability of formic acid dimer. E. A. MOELWYN-HUGHES (J.C.S., 1938, 1243).—Calculation of the contribution of the dipole-dipole interaction to the energy of formation of the H bonds in HCO_2H dimer gives vals. sufficiently close to the observed val. (cf. A., 1928, 1084) to show the importance of electrostatic effects for the stability of this intermol. complex. H. G. M.

Free acetyl. G. SEMERANO (Gazzetta, 1938, 68, 343—352).—Electrolytic reduction of Ac_2 at the dropping Hg cathode is normal in strong acid sys-

tems; the current-potential graph is consistent with the mechanism $\text{Ac}_2 + \text{H} \rightarrow \text{COMe}\cdot\text{CMe}\cdot\text{OH} \rightarrow$ the pinacol. In neutral or feebly acid systems, however, two diffusion waves are shown, in which the second corresponds with reduction of MeCHO , presumably formed by the mechanism $\text{Ac}_2 + \text{H} \rightarrow \text{MeCHO} + \text{Ac} \rightarrow \text{Ac}_2$. It is suggested that free Ac is formed at the Hg surface (by dissociation of Ac_2), and then reduced. E. W. W.

Preparation of anhydrous acetates. M. R. ADAMS and A. W. DAVIDSON (Trans. Kansas Acad. Sci., 1935, 38, 129—130).—Anhyd. acetates (e.g., of Al, Zn, Cu, Fe) are prepared by electrolysis a solution of an alkali or alkaline-earth acetate in AcOH (e.g., 10% NaOAc in AcOH) with an anode of the appropriate (activated) metal. CH. ABS. (c)

General method of testing ethyl acetate. A. BOHANES (Chem. Obzor, 1936, 11, 71—73; Chem. Zentr., 1936, ii, 2761).—20 g. of ester are hydrolysed by 2N aq. KOH overnight or with warming and excess of KOH is titrated. EtOH is determined in the distillate. A. H. C.

(A) **Synthesis and (B) relative velocities of hydrogenation of esters of oleic and elaidic acids.** A. K. PLISOV and U. P. GOLENDEEV (Rep. U.S.S.R. Fat and Margarine Inst., 1935, No. 2, 3—11, 12—21).—(A) The following esters are described: *Pr*, b.p. 216—220°/14 mm., *Pr* ^{β} , b.p. 215—217°/14—15 mm., *Bu*, b.p. 223—227°/14—15 m., *Bu* ^{β} , b.p. 220—224°/12—13 mm., and *allyl*, b.p. 218—221°/12—13 mm., *oleate*; *Bu*, b.p. 224—227°/14 mm., *Bu* ^{β} , b.p. 222—226°/12—13 mm., and *allyl*, b.p. 215—220°/13—15 mm., *elaidate*. Oxides of N (but not H_2SO_4) effect the oleic-elaidic change.

(B) Oleic esters are slightly more readily reduced (Pd) and are therefore presumed to have the *cis* configuration. CH. ABS. (c)

Catalytic hydrogenation under reduced pressure. I. **Hydrogenation under reduced pressure of arachis oil and of *p*-toluquinoline.** R. ESCOURROU (Bull. Soc. chim., 1938, [v], 5, 1184—1200).—Hydrogenation (Raney Ni on pumice) at 350°/55 mm. of arachis oil gives white fumes and a product which solidifies when cooled and contains stearic and oleic acid. At 300°/55 mm. decomp. is also observed. At about 220°/50 mm. there is no marked change but the condensable products have a strong fluorescence. Treatment at 180—190°/35 mm. results in improved odour, diminution of the I val., and constancy of the CNS val. showing thus the transformation of linoleic acid or its isomeride into oleic acid. It is therefore possible to remove those components of the oil which are least digestible and tend most strongly to become rancid without affecting the essential characteristics. Hydrogenation (Raney Ni on pumice) of 6-methylquinoline at 260°/atm. pressure is accompanied by some fission with production of NH_3 and gives mainly 6-methyl-tetra- (I) with some -deca- (II) -hydroquinoline. At 250°/40 mm. there is no trace of fission and very little (II) is formed whilst at 200°/15 mm. the sole product is (I). Ag-pumice is a much less active catalyst and (II) is never produced in its presence. There is scarcely

any fixation of H_2 in a vac. or at atm. pressure. At 400° traces of indole derivatives are formed. In presence of Pt-pumice (I) is formed exclusively; (II) is not formed at 200° /atm. pressure. H. W.

Reaction between ethyl acetoacetate and diazomethane. F. ARNDT, L. LOEWE, T. SEVERGE, and I. TÜREGÜN (Ber., 1938, **71**, [B], 1640—1644).—In the complete absence of OH-compounds reaction between $CH_3Ac \cdot CO_2Et$ and CH_2N_2 occurs very slowly. In presence of MeOH a product is obtained the % composition of which accords with that of $OMe \cdot CMe \cdot CH \cdot CO_2Et$ but it has a low OMe content. The isomeric impurity cannot be $CHMeAc \cdot CO_2Et$ since the product gives no reaction with $FeCl_3$ and gives solely $COMe_2$ when hydrolysed. It is identified as the oxide $\begin{matrix} O \\ | \\ CH_2 > CMe \cdot CH_2 \cdot CO_2Et \end{matrix}$, since treatment of the crude product with HCl and subsequent fractionation gives the *chlorohydrin*, $C_8H_{15}O_3Cl$, b.p. $75^\circ/1$ mm. H. W.

Photochemical decomposition of L-ascorbic acid. A. E. KELLIE and S. S. ZILVA (Biochem. J., 1938, **32**, 1561—1565).—Light from a Hg-vapour lamp causes the anaërobic decomp. of L-ascorbic acid (I) but not that of dehydroascorbic acid (III) in phosphate buffer solution in quartz-distilled H_2O at p_H 7. In the presence of O_2 , (I) decomposed more rapidly with ultra-violet than with visible light, particularly when a sensitiser such as methylene-blue or lactoflavin was added, formation of (II) coinciding with the disappearance of (I). In the anaërobic decomp. of (II), formation of (II) or stimulation of photochemical change by sensitisers could not be detected. Acidity retards both aërobic and anaërobic decomp. of (I) by ultra-violet light.

T. F. D.

Ketol condensation of β -keto-esters with acyclic aldehydes. H. GAULT (Congr. int. Quim. pura apl., 1934, **9**, IV, 352—359; Chem. Zentr., 1936, ii, 3295).—Reactions of $CH_3Ac \cdot CO_2Et$ with acyclic aldehydes are reviewed (cf. A., 1934, 1332). Following Gault and Wendling (A., 1935, 65; 1936, 706; cf. A., 1936, 590), 30% aq. MeCHO and $CHMeAc \cdot CO_2Et$ yield after shaking for 8 hr. with K_2CO_3 Et methyl- α -hydroxyethylacetoacetate, b.p. 118 — $120^\circ/14$ mm. A. H. C.

Chloral derivatives of lævulic acid. H. W. COLES (J. Amer. Pharm. Assoc., 1938, **27**, 477—480).—Lævulic acid (1 mol.) and chloral (1 mol.) in presence of NaOAc (1 mol.) at 100° for 4 hr. yield β -chloral-lævulic acid [γ -keto- β - β' - β'' -trichloroethylidene-n-valeric acid], m.p. 113.5° (p-nitrophenylhydrazone, m.p. 182° ; semicarbazone, m.p. 205.5 — 206° ; p-bromophenylhydrazone, m.p. 161° ; β -naphthylhydrazone, m.p. 188 — 189° ; phenylhydrazone, m.p. 174.5° ; oxime, m.p. 103 — 104° ; thiosemicarbazone, m.p. 177 — 177.5°), having no toxic or hypnotic action in rats. All m.p. are corr. F. O. H.

Oxidation of drying oils and cognate substances. IV. Properties of the ketol grouping. R. S. MORRELL and E. O. PHILLIPS (J.S.C.I., 1938, **57**, 245—247).—The equilibrium mixture of θ -hydroxy- ι -ketostearic acid (I) and ι -hydroxy- θ -ketostearic acid (II) in KOH-EtOH (cf. King, A., 1937, II, 48)

with O_2 gives nonoic and azelaic acids quantitatively. Oxidation is less complete in 40% aq. KOH. 40% methylation of the $\cdot CH(OH) \cdot$ in (I), but practically none in the case of (II), occurs with HCl in MeOH. Me_2SO_4 followed by CH_2N_2 produces $\approx 50\%$ methylation of the ketol group in (I) owing to tautomeric change. The methylation products of (I) and (II) are relatively stable to O_2 (25% oxidation in KOH-EtOH). Etherification with $(CH_3 \cdot OH)_2$ gives similar results. θ -Diketostearic acid semicarbazone, m.p. 216° (decomp.), and p-bromophenacyl nonoate, m.p. 64.5° , are recorded.

Thermal decomposition of oxalates. I. Formation of peroxides by the thermal decomposition of oxalates in a vacuum. P. L. GÜNTHER and H. REHAAG (Ber., 1938, **71**, [B], 1771—1777).—It is shown in the instance of $Nd_2(C_2O_4)_3$ that the thermal decomp. of oxalates in a vac. can lead to true peroxides which can be formally represented by the elimination of two mols. of CO from one C_2O_4 group per mol. $Nd_2(C_2O_4)_3$ thus affords Nd peroxydioxalate in 100% yield. The formation of peroxides from the oxalates of Na, Ca, Ba, and Th is established qualitatively. The production of CO_2 during thermal decomp. is due to the secondary reaction, $2CO \rightarrow CO_2 + C$. The C gives a colloidal solution when the residue from the decomp. is treated with a suitable medium. The properties of such solutions are discussed.

H. W.

Maleic acid production: vapour-phase oxidation of five-carbon olefinic acids. W. L. FAITH and M. F. YANTZI (J. Amer. Chem. Soc., 1938, **60**, 1988—1989).—Passage of $CH_3Et \cdot CH \cdot CO_2H$ or $CHMe \cdot CH \cdot CO_2Et$ with air over V_2O_5 on Al at 71.1° gives up to 38.8 and 42.2%, respectively, of maleic acid (I) and CO_2 ; other acids and aldehydes are also formed. Tiglic acid at 80.3° gives no (I). R. S. C.

Racemisation during esterification by diazomethane. E. BERGMANN and Y. SPRINZAK (J. Amer. Chem. Soc., 1938, **60**, 1998—1999).—(—)- $CO_2H \cdot CH_2 \cdot CHBr \cdot CO_2H$ and CH_2N_2 in Et_2O give the dl-ester. The acid is not racemised by Et_2O -MeOH, nor the (—)-ester by CH_2N_2 . R. S. C.

Mechanism of the cleavage of ethyl $\alpha\alpha'$ -dibromoadipate by diethylamine. R. C. FUSON and W. E. LUNDQUIST (J. Amer. Chem. Soc., 1938, **60**, 1889—1893).—Cleavage of meso- $(CH_2 \cdot CHBr \cdot CO_2Et)_2$ (I) by sec. bases is best explained as occurring by way of $\alpha\delta$ -diradicals; its occurrence depends greatly on the solvent used. Et_2 Δ^1 -cyclobutene-1:2-dicarboxylate and $NHEt_2$ in abs. EtOH at 100° gives Et_2 1-diethylaminocyclobutane-1:2-dicarboxylate, b.p. 100 — $101^\circ/2$ mm. (picrate, m.p. 125 — 130.5°), which is too stable to be an intermediate in the cleavage referred to. NH_2Et and (I) in C_6H_6 at 100° give Et_2 1-ethylpyrrolidine-2:5-dicarboxylate (II), b.p. 108 — $109^\circ/2$ mm. (platini-chloride, m.p. 132.5 — 135.5°). In EtOH (I) and $NHEt_2$ give 27% of (II), no cleavage occurring; in $COMe_2$ some, and in C_6H_6 mainly, cleavage occurs. $NHMe_2$ and (I) give 35% of $NMe \cdot \begin{matrix} CH(CO_2Et) \cdot CH_2 \\ | \\ CH(CO_2Et) \cdot CH_2 \end{matrix}$, b.p. 114 — $115^\circ/4$ mm. R. S. C.

Catalytic decarboxylation of β -keto-acids. S. KANEKO (J. Biochem. Japan, 1938, 28, 1—18).—Spontaneous decarboxylation (at 37°) of hydroxy-fumaric acid (I) at p_H 4.2 is $>$ that at p_H 1.7. Decarboxylation of (I) and hydroxymaleic acid (II) at 0° is catalysed by NH_2Ph , the optimum p_H being approx. 5.0 and 4.2, respectively. Data for the catalytic action of various org. bases on the decarboxylation of (I) and (II) at 0° and p_H 4.2—4.3 are tabulated. With (I), 4-aminoantipyrine (which also catalyses decarboxylation of $CH_3Ac \cdot CO_2H$) has the greatest catalytic action (optimum p_H 3.6—5.0), the catalysis being partly inhibited by $AcCO_2H$. F. O. H.

Typical examples of applications of polarimetry in chemistry. M. PARISELLE (Congr. int. Quim. pura apl., 1934, 9, II, 415—427; Chem. Zentr., 1936, ii, 2328).—The formation of *ferritartaric acid* (I), $C_4H_3O_6Fe$, from tartaric acid and $Fe(NO_3)_3$ is indicated by $[\alpha]$, which is max. for equimol. mixtures. The reaction is reversible but (I) is obtained on neutralising free HNO_3 as an ochre-yellow ppt. yielding a Na_1 salt. Salts $(C_4H_3O_6Na_3)Fe$ and $(C_4H_3O_6Na_2)_3Fe$ are also formed. Narcotine and hydrastine are laevorotatory in neutral, dextro- in acid or alkaline, solution.

A. H. C.

Rare-earth tartrates with antimonyl and potassium chloride.—See A., 1938, I, 501.

Synthesis of *dl*-xylomethylonic acid. O. WICHTERLE (Coll. Czech. Chem. Comm., 1938, 253—258).—Oxidation ($KMnO_4$ at 0°) of *dl*-Ca α -hydroxy- Δ^8 -pentenoate and acidification yields *dl*-xylomethylonic acid (*brucine* salt, m.p. 183—184°, $[\alpha]_D^{20}$ —25.8° in H_2O) which readily lactonises on evaporation, and is oxidised (HNO_3) to *dl*-tartaric acid; it could not be epimerised by C_5H_5N to the acid obtained by oxidising β -angelicalactone (Thiele *et al.*, A., 1902, i, 156).

A. LI.

Derivatives of glycuronic acid. IX. Synthesis of aldobionides and the relationship between the molecular rotation of derivatives of acetylated aldoses and uronic acids. W. F. GOEBEL and R. E. REEVES (J. Biol. Chem., 1938, 124, 207—220).—Me α -hepta-acetylcellobiuronate (A., 1935, 1168) in $CHCl_3$ and $AcOH \cdot HBr$ give, after removal of solvent and HBr in vac., Me α -bromohexa-acetylcellobiuronate [designated α on Hudson's nomenclature], m.p. 200° (decomp.), $[\alpha]_D^{24}$ +99.4° (all rotations in $CHCl_3$), which with Ag_2O in $MeOH \cdot CHCl_3$ gives Me hexa-acetylcellobiuronate β -methylglucoside, m.p. 200°, $[\alpha]_D^{23}$ —27.2°, or with $p\text{-NO}_2 \cdot C_6H_4 \cdot CH_2 \cdot OH$ the corresponding β -p-nitrobenzylglucoside, m.p. 199—200°, $[\alpha]_D^{23}$ —41.7°. The aldobiuronic acid of gum acacia (A., 1930, 66), 6- β -glycuronosidogalactose, is now named *acaciabiuronic acid*. Me acaciabiuronate (I) with $Ac_2O \cdot C_5H_5N$ gives the first hepta-acetate (II) (cf. A., 1938, II, 45) [converted in $Ac_2O \cdot ZnCl_2$ into a second hepta-acetate (III), m.p. 195—197°, $[\alpha]_D^{25}$ +46.5°], and a third hepta-acetate (IV), $[\alpha]_D^{25}$ +15.7°. Probably (II) and (III) are an α and β isomeric pair; (IV) may be a mixture. Me bromohexa-acetylacaciabiuronate, m.p. 201—202°, $[\alpha]_D^{23}$ +194.7° [from (II)], with $AgOAc$ in $CHCl_3$ gives a fourth hepta-acetate of (I), m.p. 110—112°, $[\alpha]_D^{23}$ +92.1°, and with Ag_2O in $CHCl_3 \cdot MeOH$ a first methylglucoside (V), m.p. 134.5°, $[\alpha]_D^{24}$ +86.4°,

of Me hexa-acetylacaciabiuronate (probably α), of which a second methylglucoside (VI), m.p. 140°, $[\alpha]_D^{23}$ —58.8°, is also obtained from acaciabiuronic acid and $MeOH \cdot HCl$, followed by acetylation. These are presumably not an α - β pair, but are of different ring structures. The velocity coeffs. of their hydrolysis suggest that the galactose portion of the acaciabiuronic acid mol. has in (V) a pyranose and in (VI) a furanose structure. Relations between $M[\alpha]$ of saccharides and of uronic acids are tabulated; their is an approx. const. change on the conversion of terminal $CH_2 \cdot OAc$ into CO_2Me . E. W. W.

Excretion of menthoglycol glycuronate by rabbits after consumption of citronellal. R. KUHN and I. Löw (Z. physiol. Chem., 1938, 254, 139—143; cf. A., 1937, II, 321; Barbier and Leser, A., 1897, i, 537).—The urine of rabbits given an aq. emulsion of citronellal or menthane-3:8-diol by stomach tube contains the d-glycuronate, $C_{16}H_{28}O_8 + H_2O$, m.p. 192° (decomp.), $[\alpha]_D^{25}$ —15.2° in $EtOH$ of the diol (Me ester, m.p. 193—194°, + $\frac{1}{3}MeOH$, m.p. 196°, $[\alpha]_D^{20}$ —10° in $EtOH$, and its triacetate, m.p. 171—172°, $[\alpha]_D^{20}$ —20° in $CHCl_3$ [Ac groups in the glycuronic acid residue]; p-bromophenacyl ester, $C_{24}H_{31}O_9Br + H_2O$, m.p. 189°, the acid being united to the diol through its sec. OH. The diol is obtained from citronellal by shaking for 48 hr. at 37° with 0.5% HCl . W. McC.

Preparation of d-galacturonic acid from d-galactose. H. M. SELL and K. P. LINK (J. Amer. Chem. Soc., 1938, 60, 1813—1814).—Prep. of diisopropylidene-d-galactose (when pure, has b.p. 130—140°/0.01—0.001 mm., $[\alpha]_D^{20}$ —54.7° in $CHCl_3$) from α -d-galactose, and of K diisopropylidene-d-galacturonate, m.p. 200—205° (decomp.), $[\alpha]_D^{20}$ —61.1° in H_2O , the free acid, m.p. 157°, $[\alpha]_D^{25}$ —84°, and d-galacturonic acid, decomp. 159—160° (sinters at 110—111°), $[\alpha]_D^{20}$ +98° \rightarrow 50.9° in H_2O , therefrom is improved to give 76—92, 49—65, 78—88, and 65—81% yield, respectively. R. S. C.

Constitution of thio-acids.—See A., 1938, I, 434.

Polymerisation and condensation of formaldehyde in heavy water. W. D. WALTERS (Z. physikal. Chem., 1938, 182, 275—277).—Polymerisation of CH_2O in D_2O in presence of H_2SO_4 or KOH leads to inclusion of no D in the α -polyoxymethylene. Condensation of CH_2O in aq. $MeOH$ in presence of CaO yields sugars which contain about 8.2% of D which cannot be removed by washing. Replacement of $MeOH$ by $MeOD$ increases this amount to 16.7%. The exchange of D for H is supposed to occur during enolisation of the intermediate aldehydes and ketones. J. W. S.

Reduction of acetaldehyde at the dropping mercury cathode.—See A., 1938, I, 465.

Structure of the aldol of acetaldehyde. M. BACKÈS (Compt. rend., 1938, 207, 74—76; cf. A., 1935, 962).—Spectroscopic observations show that the aldol probably does not exist in an epoxy-form. In C_6H_6 it shows a band at 9674 Å., characteristic of a tert.-OH. The polymeride does not exhibit this band, which indicates that polymerisation occurs through the tert.-C. The Raman spectra of

the monomeride and freshly formed dimeride in the absence of a solvent are the same, but on keeping at a temp. $>$ its m.p., the latter shows additional weak lines. The spectra show lines characteristic of the linkings C-C, C-H, and C-OH, a line at 1150 cm^{-1} probably due to the CHO and C-OH arrangements at one C, and a line at 1206 cm^{-1} due to CO classified as carbonyl XII which differs from a "normal" and an "active" CO. J. L. D.

Polycondensation of acraldehyde. E. E. GILBERT and J. J. DONLEAVY (J. Amer. Chem. Soc., 1938, 60, 1911—1914).—In presence of dil. aq. NaOH acraldehyde (I) gives an amorphous "pentameride" (II), $\text{OH}\cdot[\text{CH}_2\cdot\text{CH}(\text{CHO})]_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$ (tetra-2:4-dinitrophenylhydrazones, decomp. about 120°), by hydration followed by Michael addition of (I). Oxidation of (II) gives a polyacrylic acid, sinters at about 70° . (I) and (II) are in equilibrium, since the rate of formation of (II) depends on the concn. of NaOH, but the amount formed depends on the temp., a lower temp. favouring formation of (II). (I) polymerises more readily than does $\text{CH}_2\cdot\text{CMe}\cdot\text{CHO}$ (cf. following abstract) since the latter gives mainly the trimeride. R. S. C.

Polycondensation of α -methylacraldehyde. E. E. GILBERT and J. J. DONLEAVY (J. Amer. Chem. Soc., 1938, 60, 1737—1738).—In presence of NaOH in aq. EtOH $\text{CH}_2\cdot\text{CMe}\cdot\text{CHO}$ (I) condenses by addition of H_2O to give $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CHO}$, Michael addition of (I) thereto at the active CH to give $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}(\text{CHO})\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CHO}$, and further similar addition to give, as the product isolated, the trimeride, $\text{OH}\cdot\text{CH}_2[\text{CMe}(\text{CHO})\cdot\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{CHO}$, b.p. $113\text{—}118^\circ/12\text{ mm.}$ (tris-2:4-dinitrophenylhydrazones, m.p. $173\text{—}174^\circ$). Reaction proceeds similarly further, yielding also small amounts of the tetrameride, b.p. $159\text{—}164^\circ/12\text{ mm.}$, and pentameride, b.p. $175\text{—}180^\circ/9\text{ mm.}$ (tris-2:4-dinitrophenylhydrazones, decomp. about 100°). R. S. C.

Condensation of *n*-butaldehyde with butan- β -one. II. S. G. POWELL and D. A. BALLARD (J. Amer. Chem. Soc., 1938, 60, 1914—1916; cf. A., 1925, i, 7).—Condensation of Pr^nCHO and COMeEt by 2.5% NaOH gives $\text{CHPr}^n\cdot\text{CMe}\cdot\text{COMe}$ and $\text{CHBu}^n\cdot\text{CEt}\cdot\text{CHO}$ (I), which are separable only with difficulty. Similarly, Eccott and Linstead's substance (semicarbazone, m.p. 152°) (A., 1930, 893) obtained from Pr^nCHO and COMe_2 is (I). γ -Methyl- Δ^7 -hepten- β -one-2:4-dinitrophenylhydrazone, m.p. 137° , β -ethyl- Δ^6 -hexen- α -al-2:4-dinitrophenylhydrazone, m.p. $124\text{—}125^\circ$, and α -methyl- Δ^6 -hexeno-*p*-toluidide, m.p. $85\text{—}88^\circ$, are described. R. S. C.

Aldehydes and hydroxyaldehydes of the polymethylene series. VII. By-products of synthesis of ethyl tetramethylenedicarboxylate by Kishner's method. E. D. VENUS-DANILOVA (J. Gen. Chem. Russ., 1938, 8, 477—483).—In the prep. of Et cyclobutanedicarboxylate from $\text{CHNa}(\text{CO}_2\text{Et})_2$ and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Br}$ Et₂ di- γ -chloropropylmalonate (I), m.p. $52\text{—}53^\circ$, is obtained as a by-product. (I) and NaOEt in EtOH (2 hr. at the b.p.) yield the di- γ -lactone of di- γ -hydroxypropylmalonic acid (II), m.p. $49\text{—}51^\circ$, hydrolysed by boiling

aq. $\text{Ba}(\text{OH})_2$ to the Ba salt of the corresponding mono- γ -lactone (III). (I) and (III) are also isolated from the acid fraction of the reaction product obtained by Kishner's method. A further by-product is EtOAc, formed by decarboxylation of $\text{CH}_2(\text{CO}_2\text{Et})_2$. R. T.

Preparation of *l*-glyceraldehyde. E. BAER and H. O. L. FISCHER (Science, 1938, 88, 108).—*l*-Glyceraldehyde has been prepared in the following way: *l*-arabinose \rightarrow *l*-mannonolactone \rightarrow *l*-mannitol \rightarrow 1:2:5:6-diisopropylidene-*l*-mannitol \rightarrow isopropylidene-*l*-glyceraldehyde \rightarrow *l*-glyceraldehyde (2:4-dinitrophenylhydrazone, m.p. 148° ; dimedon compound, m.p. $198\text{—}200^\circ$, $[\alpha]_D^{25} -198^\circ$ in EtOH). The optical rotations of *l*- and *d*-glyceraldehyde decrease in aq. solution on keeping from -14° to -7° and from $+14^\circ$ to $+7^\circ$, respectively. The CHO content of the solution remains unchanged, and the higher-rotating forms of both aldehydes can be regained by evaporation. L. S. T.

Relations of *cis-trans* isomerism to asymmetric oxidation of sugars. M. R. EVERETT and F. SHEPPARD (J. Amer. Chem. Soc., 1938, 60, 1792—1796).—The relative behaviour of sugars to Sumner's dinitrosalicylate and the Folin-Wu Cu reagent containing *d*-, *l*-, or *meso*-tartaric acid depends on the nature and stereochemistry of the ring. *cis-trans* Relations often have a predominating effect, but no completely comprehensive rules are found. R. S. C.

Nomenclature of higher monosaccharides. E. VOTOČEK (Coll. Czech. Chem. Comm., 1938, 264—272).—A new system is proposed. A. LI.

2:4:6-Trimethylgalactose and its α - and β -methylgalactosides. D. J. BELL and S. WILLIAMSON (J.C.S., 1938, 1196—1200).—2:4:6-Trimethylgalactose (I), m.p. $102\text{—}105^\circ$, $[\alpha]_D^{25}$ (initial) $+124^\circ$, (at equilibrium) $+90.4^\circ$, has been synthesised by two methods and is identical with that isolated by Percival *et al.* (A., 1937, II, 445) from agar. 2-Methyl- β -methylgalactoside (simplified prep. described, based on the facile formation of 3:4-isopropylidene- β -methylgalactoside from the galactoside and $\text{COMe}_2\text{--H}_2\text{SO}_4$) with PhCHO and anhyd. ZnCl_2 gives 4:6-benzylidene-2-methyl- β -methylgalactoside, m.p. 160° , $[\alpha]_D^{25} -32.8^\circ$ (cf. A., 1938, II, 127), the 3-*p*-toluenesulphonyl derivative, m.p. 126° , $[\alpha]_D^{25} +38.4^\circ$, of which when hydrolysed with $\text{HCl--COMe}_2\text{--H}_2\text{O}$ and then methylated with Purdie's reagents gives 2:4:6-trimethyl- β -methylgalactoside 3-*p*-toluenesulphonate, m.p. 130° , $[\alpha]_D^{25} +20.4^\circ$. This with NaOMe-MeOH (90° ; 14 hr.) gives 2:4:6-trimethyl- β -methylgalactoside, m.p. $111\text{—}112^\circ$, $[\alpha]_D^{25} -40.9^\circ$, converted by 0.33N-HCl at the b.p. into (I). α -Methylgalactoside 6-*p*-toluenesulphonate when condensed with COMe_2 and then methylated by Purdie's method gives 2-methyl-3:4-isopropylidene- α -methylgalactoside 6-*p*-toluenesulphonate, m.p. 90° , $[\alpha]_D^{25} +90.9^\circ$, which when boiled with $\text{NaOH--H}_2\text{O--EtOH}$ (36 hr.) gives 2-methyl-3:4-isopropylidene- α -methylgalactoside (II), m.p. $77\text{—}78^\circ$, $[\alpha]_D^{25} +157.4^\circ$, which when methylated by Purdie's reagents gives 2:6-dimethyl-3:4-isopropylidene- α -methylgalactoside, b.p. $120/0.1\text{ mm.}$, $[\alpha]_D^{25} +155^\circ$ in H_2O , $n_D^{20} 1.4550$. This is hydrolysed

by 5% HCl to 2:6-dimethyl- β -galactose and converted by fuming HNO_3 in dry CHCl_3 into 2:6-dimethyl- α -methylgalactoside 3:4-dinitrate, m.p. 50–51°, $[\alpha]_D^{20} +160.7^\circ$. When boiled with 10% aq. AcOH , (II) gives 2-methyl- α -methylgalactoside, $[\alpha]_D^{20} +180^\circ$ in MeOH , which did not crystallise, hydrolysed to 2-methyl- β -galactose, and with PhCHO and anhyd. ZnCl_2 gave 4:6-benzylidene-2-methyl- α -methylgalactoside, m.p. 152°, $[\alpha]_D^{20} +131.6^\circ$. This was converted into its 3-*p*-toluenesulphonyl derivative, m.p. 145°, $[\alpha]_D^{20} +158.4^\circ$, which when hydrolysed with $\text{HCl}-\text{COMe}_2-\text{H}_2\text{O}$ and then methylated with Purdie's reagents gives 2:4:6-trimethyl- α -methylgalactoside 3-*p*-toluenesulphonate, m.p. 112°, $[\alpha]_D^{20} +150.0^\circ$, with some strongly reducing material. The former with $\text{NaOMe}-\text{MeOH}$ (90°; 72 hr.) gives 2:4:6-trimethyl- α -methylgalactoside, m.p. 73–74°, $[\alpha]_D^{20} +163.9^\circ$ in H_2O , which is very hygroscopic and is hydrolysed by dil. HCl to (I). Except where otherwise stated, all $[\alpha]$ were measured in CHCl_3 . Hydrolysis of the *p*- $\text{C}_6\text{H}_4\text{Me}-\text{SO}_2$ groups took place in accord with previous conclusions (A., 1935, 963), that Walden inversion does not occur when the formation of an anhydro-ring is inhibited by suitable substitution of the remaining OH groups in the sugar. In the present examples such inhibition greatly reduced the ease of hydrolysis. H. G. M.

β -Fucohexose and β -fucohexitol. E. VOTOČEK (Coll. Czech. Chem. Comm., 1938, 273–277; cf. A., 1938, II, 127).— β -Fucohexonolactone is reduced (Na-Hg) to β -fucohexose, $[\alpha]_D$ (after 30 hr.) $+59.7^\circ$ in H_2O [phenylhydrazine, m.p. 163°; phenylosazone, m.p. 202° (decomp.); phenylbenzylhydrazine, m.p. 168° (decomp.)], further reduced to β -fucohexitol, m.p. 150°, $[\alpha]_D 0^\circ$ in H_2O (tribenzylidene derivative, m.p. 186–187°). A. LI.

Colouring matter of Indian tulip (*Thespesia populnea*) flowers: populnin and populnetin. K. NEELAKANTAM and T. R. SESHADRI (Current Sci., 1938, 7, 16–17).—The petals of this flower, collected in Coimbatore in October, contained populnetin (I), $\text{C}_{14}\text{H}_{18}\text{O}_6$, m.p. 270–275° (Ac_4 derivative, m.p. 127–129°), a smaller amount of populnin (II), m.p. 228–230° (decomp.) [the glucoside of (I)], and a trace of a substance (Ac derivative, m.p. 182–185°). Collected in Trichinopoly in the summer, the petals contained only (II). Colour reactions indicate that (I) is a tetrahydroxyanthraquinone. R. S. C.

N-Glucosides. I. Toluidino- and xyloidino-N-glucoside. K. HANAOKA (J. Biochem. Japan, 1938, 28, 109–118).—The following were prepared by Kuhn and Dansi's method (A., 1936, 1095): *o*-, m.p. 101° (–99.0, –51.0; –103.0, –22.0) and *p*-toluidino-, m.p. 115° (–106.0, –50.0; –87.0, –35.0), *m*-toluidino-, m.p. 117° (–102.9, –50.3; –102.0, –32.0), and 1:2:3-, m.p. 154–155° (–104.0, –46.0; –88.0, –30.0), *p*-, m.p. 95–97° (–102.5, –45.0; –103.5, –25.0), *as-o*-, m.p. 110–111° (–92.5, –41.5; –79, –29.5), *s-m*-, m.p. 145° (–102.5, –44.0; –96.0, –30.0), and *as-m*-xyloidino-glucoside, m.p. 105–106° (–101.0, –45.0; –95.0, –25.0). Vals. in parenthesis are for $[\alpha]_D^{20}$ in degrees, initially and after mutarotation, in MeOH and EtOH , respectively. Data for the rate of hydrolysis in dil.

H_2SO_4 at 23° indicate that the greater is the proximity of NH_2 and Me groups of the aglucone, the greater is the tendency of the corresponding glucoside to resist acid hydrolysis. F. O. H.

Nitrogenous glucosides. IV. Attempts to synthesise pyrimidine glucosides. T. B. JOHNSON and W. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 1916–1918; cf. A., 1935, 69).—Attempts to utilise carbamido-derivatives of sugars for the synthesis of pyrimidine glucosides failed. Bromotriacetarabinose and AgNCO in boiling xylene give a product, deacetylated by conc. aq. NH_3 to *l*-arabinosylcarbamide, m.p. 192°, $[\alpha]_D^{20} +51.9^\circ$ in H_2O . Bromotriacetoxylucose gives similarly *s*-dixylosylcarbamide, decomp. 230–250°, $[\alpha]_D^{20} -20.5^\circ$ in H_2O . Bromohepta-acetyl-lactose and AgNCS in boiling xylene give hepta-acetyl-lactosylthiocarbimide, m.p. 169–170°, converted by EtOH into *Et* hepta-acetyl-lactosylthiourethane, $+x\text{H}_2\text{O}$, m.p. 119°, and by $\text{CO}_2\text{Et}-\text{CH}_2-\text{NH}_2-\text{HCl}$ and a little $\text{C}_2\text{H}_5\text{N}$ in CHCl_3 into *Et* hepta-acetyl-lactosylureidoacetate, m.p. 100°. Tetra-acetylglucosylcarbamide (I), $\text{CN}-\text{CH}_2-\text{CO}_2\text{H}$, and Ac_2O at 100° give *N*-tetra-acetylglucosyl-*N'*-cyanoacetylcarbamide, m.p. 135° (oximino-derivative, m.p. 179–180°), hydrolysed by NH_3 to glucosylcarbamide (I), $\text{CH}_2(\text{CO}_2\text{H})_2$, and Ac_2O at 100° give malonylbistetra-acetylglucosylcarbamide, m.p. 206–207°. R. S. C.

Constitution of damson gum. I. Composition of damson gum and structure of an aldobionic acid (glycuronosido-2-mannose) derived from it. E. L. HIRST and J. K. N. JONES (J.C.S., 1938, 1174–1180).—The crude gum (neutral salt of metallic radicals) is purified and obtained ash-free as an acidic polysaccharide (I), $[\alpha]_D^{20} -26^\circ$ (as Na salt in H_2O) (TI salt and insol. TI complex), of equiv. wt. about 1100. Analysis gives 16.4% of uronic anhydride and 36.2% of araban. Autohydrolysis of (I) occurs when it is heated with H_2O (90–95°; 24 hr.), and gives *l*-arabinose, *d*-galactose (II) (trace), and a polysaccharide (A) (III), insol. in EtOH , and containing a repeating unit of *d*-glycuronic acid (IV) (1 mol.), *d*-mannose (1 mol.), *d*-galactose (2 mols.). The repeated unit of (I) contains in addition *l*-arabinose (3 mols.). When boiled with 2*N*- H_2SO_4 for 6.5 hr. (III) gives (II) and an aldobionic acid, shown to be β -*d*-glycuronosido-2-*d*-mannose, and obtained as the impure Ba salt (V), $[\alpha]_D^{20} -16^\circ$ in H_2O , mixed with a little (IV). With boiling 2*N*- H_2SO_4 (22 hr.) (V) is split, giving equal proportions of *d*-glycuronic acid and *d*-mannose. Methylation of (V) with $\text{Me}_2\text{SO}_4-\text{NaOH}$, followed by esterification with MeI and Ag_2O , gives the *Me* ester of heptamethyl- β -*d*-glycuronosido-2-*d*-mannopyranose, b.p. 175°/0.002 mm., n_D^{20} 1.4675, $[\alpha]_D^{20} -16^\circ$ in H_2O , together with a little *Me* tetramethyl-*d*-glycuronate. Hydrolysis of the former with 7% HCl (90–95°; 6.5 hr.) gives an equimol. mixture of 2:3:6-trimethyl-*d*-glycuronic acid (VI) and 3:4:6-trimethyl-*d*-mannose (A., 1930, 1024), oxidised by $\text{Br}-\text{H}_2\text{O}$ to 3:4:6-trimethylmannolactone (cf. *loc. cit.*), which with liquid NH_3 gives 3:4:6-trimethyl-*d*-mannonamide, m.p. 141°, $[\alpha]_D^{20} +25^\circ$. This gave a strong positive Weerman reaction (cf. A., 1917, i, 546) with NaOCl , indicating the presence of $\cdot\text{OH}$ in C_{62} . Oxidation of (VI) with $\text{Br}-\text{H}_2\text{O}$ (60°; 8 hr.) gives 2:3:4-trimethyl-

saccharic acid, identified as the Me ester of 2:3:4-trimethylsaccharolactone (A., 1932, 45). After simultaneous esterification and glycoside formation (VI) gives the Me ester, b.p. $140^{\circ}/0.001$ mm., $[\alpha]_D +31^{\circ}$ in H_2O , of 2:3:4-trimethyl-*d*-glycuronoside, converted by $MeOH-NH_3$ into the corresponding amide, m.p. 158° , $[\alpha]_D +60^{\circ}$ in H_2O , which is a mixture of α - and β -forms not separable by crystallisation. Hydrolysis of the methylated derivative of (III) gives a little 2:3:4-trimethylxylose. H. G. M.

Hydrolysis of starch by sweet potato amylase. K. V. GIRI (J. Indian Chem. Soc., 1938, 15, 249—262).—Sweet potato amylase resembles the β -amylase of barley in giving the same saccharification limit to Zulkowsky's sol. starch hydrolysis and the residual material resembles the erythrogranulose fraction of starch after hydrolysis by α - and β -amylases. The course of the hydrolysis of amyloamylose by sweet potato amylase also follows the same course as that found by Samec (A., 1935, 1415) for β -amylase. Van Klinkenberg's views on the composition of starch (cf. A., 1932, 1062; 1933, 92) are considered untenable. F. R. G.

Schardinger dextrans from starch. K. FREUDENBERG and M. MEYER-DELIUS (Ber., 1938, 71, [B], 1596—1600).—The prep. of methyl- α - (I), m.p. $208-210^{\circ}$, $[\alpha]_D +162^{\circ}$ in $CHCl_3$, and β - (II), m.p. $156-158^{\circ}$, $[\alpha]_D +157^{\circ}$ in $CHCl_3$, -dextrin is described. (I), (II), and α -dextrin (III) in H_2O give an intense red-brown colour whilst free β -dextrin (IV) gives a brown ppt. During hydrolysis of (I) and (II) by 34% HCl, α_D which is positive throughout increases to a max. and diminishes ultimately to the val. shown by 2:3:6-trimethylglucose in 34% HCl. Similar observations are made in 51% H_2SO_4 . Hydrolysis and subsequent glucosidation of (I) and (II) gives 2:3:6-trimethylmethylglucoside in about 95% yield. The formation of tetramethylmethylglucoside could not be detected so that trimethylglucose is the sole product. The optical behaviour shows that the majority of the linkings are similar to those in maltose. The possibility of β -linkings resembling those of cellobiose is excluded since the initial increase in α_D takes place more rapidly than the fission of the remaining linkings. The possibility of a gentiobiose linking is excluded since if present the hydrolytic product would contain 2:3:4-trimethylglucose, the 6-*p*-toluenesulphonate of which would react with NaI in warm $COMe_2$ giving the 6-iodohydrin with separation of $p-C_6H_4MeSO_3Na$; this does not occur. The sole possibility therefore is that (III) and (IV) are composed of 5 or 6 glucose units united in rings and connected with each other exclusively by linkings of the maltose type. It is concluded that during the hydrolysis of (I), (II), (III), and (IV) the initial increase in α_D is due to ring-opening the rate of which greatly exceeds that of the decomp. of the open chains; after initial rise the graph therefore resembles the falling curve of the hydrolysis of starch or methylstarch. During acetolysis, ring-opening again causes an initial increase of α_D but the rate of change does not differ markedly from that of the acetolysis of open chains so that during the whole course of acetolysis of the dextrin acetates an increase in α_D is observed. Rönt-

gen data of (III) are in harmony with a ring structure. H. W.

Effect of acetylation on the molecular chain-length of starch. R. S. HIGGINBOTHAM and W. A. RICHARDSON (J.S.C.I., 1938, 57, 234—200).—Acetates have been prepared from potato starch (Cu-reducing power, R_{Cu} , 3.0 mg. per g.) by two methods, the catalysts used being either a mixture of SO_2 and Cl_2 (acetates I) or C_5H_5N (acetates II). Acetates from starches modified by treatment with cold aq. HCl for various periods, and ranging in R_{Cu} from 4.5 to 259 (acetates III), have been prepared in presence of C_5H_5N . After deacetylation the R_{Cu} of (II) and (III) were almost unchanged, whereas those of (I) were increased by 20—50 mg. per g. The viscosities of (I) were much lower in $C_2H_2Cl_4$ than those of (II) and were within the range covered by those of (III). (I) were degraded during prep., (II) were not. Since the methylated starches used to determine chain-length (A., 1932, 1116; 1935, 1226) were obtained from acetates prepared similarly to (I), the chain-length of 24—30 glucose units calc. from the yield of tetramethylglucose does not represent that of the original starch. The average chain-length calc. from R_{Cu} ranges from 17 to 1370 units and is almost a linear function of η , but the factor of proportionality differs according to the type of distribution of chain-lengths within the single samples of starch. W. A. R.

Composition of sugar humin. A. SCHWEIZER (Rec. trav. chim., 1938, 57, 886—890; cf. A., 1938, II, 220).—Sugar humin gives good analyses for $(C_{12}H_8O_4)_n$ after drying in N_2 at $100-105^{\circ}$. A. LI.

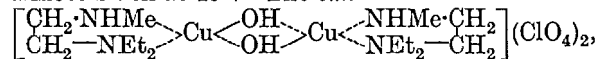
Optical properties of cellulose dispersed in cuprammonium hydroxide solution.—See A., 1938, I, 513.

Action of dilute acids on cellulose nitrates. Steric hindrance. J. DESMAROUX (Compt. rend., 1938, 206, 1483—1484).—Equiv. concns. of HNO_3 , HCl, and H_2SO_4 at $50-60^{\circ}$ hydrolyse cellulose nitrate to different extents, HNO_3 most and H_2SO_4 least easily. The different degrees of hydrolysis depend on the stereochemical configuration of the anions of the acids. J. L. D.

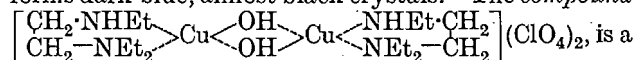
Structure from the solubility of denitrated cellulose nitrates. M. MATHIEU and (MLLE.) T. PETITPAS (Compt. rend., 1938, 206, 1485—1486).—Cellulose trinitrate (I) containing 13.8—14.0% of N with 4.66N- HNO_3 at 50° loses N as the hydrolysis continues. Simultaneously, there is no large increase in the $Et_2O-EtOH$ -sol. $(NO_2)_2$ -fraction. (I) and its hydrolytic products containing down to 11.94% of N show the X-ray diagram of (I), which explains the relative insolubility of partly hydrolysed (I). J. L. D.

Complex salts of copper with N-alkylated ethylenediamines. P. PFEIFFER and H. GLASER (J. pr. Chem., 1938, [ii], 151, 134—144).—The tendency of N-alkylated ethylenediamines to form complex salts is much less pronounced than that of $(CH_2NH_2)_2$. $CuSO_4$, $(CH_2NH_2)_2 \cdot H_2O$, and $NaClO_4$ give the blue-violet salt, $[Cu en_2](ClO_4)_2$. The blue-violet compound, $[Cu(NHMe \cdot CH_2 \cdot CH_2 \cdot NH_2)_2](ClO_4)_2$,

is obtained from the amine and $\text{Cu}(\text{ClO}_4)_2$ in MeOH ; the substance, $[\text{Cu}(\text{NHEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2](\text{ClO}_4)_2$, is obtained similarly in blue-violet crystals. The compound, $[\text{Cu}(\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2](\text{ClO}_4)_2$ forms ruby-red crystals which become violet at $43\text{--}45^\circ$ and almost black at 45° . The salt



best obtained from the amine and $\text{Cu}(\text{ClO}_4)_2$ in MeOH , forms dark blue, almost black crystals. The compound



is a blue-violet, cryst. powder which becomes red in liquid air; the transition temp. is -100° to -120° . Attempts to obtain a complex Cu salt from $\text{NHPh}\cdot[\text{CH}_2]_2\cdot\text{NEt}_2$ were fruitless, the greenish ppts. becoming brown and ultimately resinous. The praseo-salt $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ is converted by $(\text{CH}_2\cdot\text{NH}_2)_2$ into the compound, $[\text{Co en}_2\text{Cl}_2\cdot 3\text{H}_2\text{O}]$, also obtained by use of $\text{NH}_2\text{Et}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$ or from chloropentamminecobaltic chloride and $(\text{CH}_2\cdot\text{NH}_2)_2\cdot\text{H}_2\text{O}$; when heated with $\text{NHMe}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$ or $\text{NEt}_2\cdot[\text{CH}_2]_2\cdot\text{NH}_2$ the purpureo-chloride evolves NH_3 but does not appear to give a complex salt. Trichlorotripyridine-chromium and $(\text{CH}_2\cdot\text{NH}_2)_2\cdot\text{H}_2\text{O}$ give the compound, $[\text{Cr en}_2]_3\text{Cl}_3\cdot n\text{H}_2\text{O}$; complex salts could not be obtained with $\text{NEt}_2\cdot[\text{CH}_2]_2\cdot\text{NH}_2$, $\text{NH}_2\text{Et}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$, or $\text{NHMe}\cdot[\text{CH}_2]_2\cdot\text{NEt}_2$. H. W.

Hexamethylenetetramine mandelate. Preparation and toxicity. H. G. KOLLOFF and J. W. NELSON (J. Amer. Pharm. Assoc., 1938, 27, 603—605).— $(\text{CH}_2)_6\text{N}_4$ with $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ in H_2O affords hexamethylenetetramine mandelate, m.p. $130\text{--}132^\circ$; the salt is well tolerated in doses of 2—5 g. per kg. by rats. F. O. H.

New type of isomerisation and its application to the preparation of esters of amino-alcohols. H. HORENSTEIN and H. PHÄLICHE (Ber., 1938, 71, [B], 1644—1657).—Treatment of the Ag salt of an org. acid with $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{NMe}_2\cdot\text{Br}$ gives the corresponding trimethyl- β -bromoethylammonium salt, which is isomerised when heated to the methobromide of the β -dimethylaminoethyl ester. The reaction can be extended to the Cl-derivatives of other *tert*-amines and the isolation of the intermediate salts is not invariably necessary. Partial esterification of polybasic acids is possible. With inorg. acids the change appears to follow a more complex course. β -Dimethylaminoethyl lactate methobromide is obtained (79% yield) in colourless, hygroscopic crystals when aq. solutions of $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{NMe}_2\cdot\text{Br}$ and Ag lactate are mixed, AgBr and solvent are removed and the residue is heated for 6 hr. at about 90° . Corresponding salts, m.p. $152\text{--}154^\circ$, —, $210\text{--}212^\circ$, $232\text{--}234^\circ$ (decomp.), and $236\text{--}238^\circ$ (decomp.), respectively are obtained from mandelic, pyruvic, phenylquinoline-carboxylic, deoxycholic, and cholic acid.

$\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{NMe}_2\cdot\text{Br}$ and AgCNS yield trimethyl- β -thiocyanoethylammonium bromide. Diethyl- β -thiocyanoethylammonium chloride is obtained when $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{NEt}_2$ is neutralised with HCNS in EtOH and the product is heated at $90\text{--}95^\circ$. In boiling Pr^iOH $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ and $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{NEt}_2$ afford diethylaminoethyl benzoate hydrochloride, m.p. 173--

$174\text{--}5^\circ$ (corresponding base, m.p. $50\text{--}51^\circ$), also obtained from $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{Na}$ and $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{NEt}_2\cdot\text{HCl}$ at 140° . β -Piperidinoethyl benzoate hydrochloride, m.p. 176° , diethylaminoethyl salicylate hydrochloride, m.p. $144\text{--}145^\circ$, and γ -diethylaminopropyl cinnamate hydrochloride, m.p. $131\text{--}133^\circ$, are described. Diethylaminoethyl mandelate and its hydrochloride are non-cryst. γ -Diethylamino- $\beta\beta$ -dimethylpropyl dl-tropate has m.p. $138\text{--}140^\circ$. Na_2 adipate and $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{NEt}_2\cdot\text{HCl}$ at 110° afford β -diethylaminoethyl H adipate hydrochloride, which is an acidic resin. β -Diethylaminoethyl H phthalate hydrochloride is described. Partial isomerisation of the product from $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{NEt}_2$ yields diethylaminoethyl p-nitrobenzoate p-nitrobenzoate, decomp. $125\text{--}129^\circ$. H. W.

Esters of choline. A. CONTARDI and A. ERCOLI (Congr. int. Quim. pura apl., 1934, 9, V, 163—173; Chem. Zentr., 1936, ii, 3903).—The following esters were made by esterifying the appropriate acid with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ and heating the ester with NMe_3 : formylcholine chloride (β -chloroethyl formate, b.p. $132^\circ/764$ mm.); propionylcholine chloride [aurichloride, m.p. $131\text{--}132^\circ$; platinichloride, m.p. $241\text{--}5^\circ$ (decomp.)] (β -chloroethyl propionate, b.p. $162\text{--}164^\circ/763$ mm.); oxalylcholine chloride (aurichloride, m.p. $256\text{--}5^\circ$) (β -chloroethyl oxalate, m.p. 45°); acetylcarbamylcholine chloride (β -chloroethyl acetamidoformate, m.p. $73\text{--}74^\circ$); methylenedicarbamylcholine dichloride (platinichloride, m.p. 230°) (β -chloroethyl NN'-methylenebisaminoformate, m.p. 148°); methylenecarbamylcholine chloride (β -chloroethyl methyleneaminoformate); phenylmethylcarbamylcholine chloride (platinichloride, m.p. 222° ; aurichloride, m.p. 190°) (β -chloroethyl methylphenylaminoformate, b.p. $165^\circ/8$ mm.); chlorotrimethylcarbamylcholine chloride (aurichloride, m.p. 273°) (β -chloroethyl trimethylaminoformate, m.p. $<300^\circ$); iminodicarboxyldicholine dichloride [aurichloride, m.p. 240° (decomp.)]; platinichloride, m.p. 248° (decomp.)] [*di*(chloroethyl) iminodicarboxylate, m.p. 202°]. A. H. C.

Onium compounds. XIX. Thio-esters of choline and β -methylcholine and their physiological activity. R. R. RENSHAW, P. F. DREISBACH, M. ZIFF, D. GREEN, and (in part) J. H. WILLIAMS (J. Amer. Chem. Soc., 1938, 60, 1765—1770; cf. A., 1938, II, 224).—The additive compound, m.p. $201\text{--}202^\circ$, of $\text{CHMeCl}\cdot\text{CH}_2\cdot\text{NMe}_2\cdot\text{HCl}$ and $\text{CS}(\text{NH}_2)_2$ with aq. KOH gives dimethyl- β -thiolpropylamine (I), b.p. $153\text{--}154^\circ/762$ mm. [picrate, m.p. $159\text{--}166^\circ$ (decomp.) after softening; HgCNS salt, decomp. from 125°]. With a slight excess of KOH, however, it gives mainly di-(β -dimethylaminoisopropyl) disulphide, b.p. $151\text{--}154^\circ/14$ mm. [dimethiodide, m.p. $207\text{--}208^\circ$ (decomp.)]. With MeI in Et_2O , C_6H_6 , or PhMe at room temp. (I) gives a salt, $\text{C}_7\text{H}_{18}\text{NSI}$, decomp. $197\text{--}200^\circ$, not identical with that of Mylius (A., 1916, i, 633). With the acyl chloride in Et_2O (I) gives dimethyl- β -acet-, m.p. $91\text{--}92^\circ$, β -benz-, m.p. $122\text{--}5^\circ$, and β -p-nitrobenz-, m.p. $199\text{--}200^\circ$, -thiolpropylammonium chloride, converted by way of the free bases (which are very readily hydrolysed) into trimethyl- β -acet- (II), m.p. $144\text{--}145^\circ$, β -benz-, m.p. $185\text{--}186^\circ$, and β -p-nitrobenz-thiolpropylammonium iodide, m.p. $190\text{--}191^\circ$. Dimethyl- β -p-nitrobenzthiol-

propylamine has m.p. 85°. The additive compound, m.p. 181—182°, of $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{NMe}_2 \cdot \text{HCl}$ and $\text{CS}(\text{NH}_2)_2$ similarly leads to $\text{SH} \cdot [\text{CH}_2]_2 \cdot \text{NMe}_2$, ($\text{S} \cdot [\text{CH}_2]_2 \cdot \text{NMe}_2$)₂, dimethyl- β -acet-, m.p. 95°, -benz-, m.p. 164.5—165°, and *p*-nitrobenz-thioethylammonium chloride, m.p. 187° (decomp.), trimethyl- β -acet- (III), m.p. 203—204°, -benz-, decomp. about 257°, and *p*-nitrobenz-thioethylammonium iodide, m.p. 212—216° (decomp. from 195°). (II), (III), and $\text{SMe} \cdot [\text{CH}_2]_2 \cdot \text{NMeI}$ have pharmacological effects similar to those of choline, but weaker; the relatively large effect of (II) is contrary to experience in the S-free series. R. S. C.

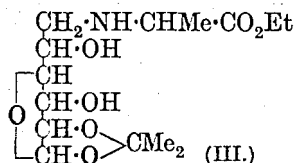
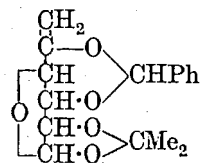
Synthesis of proteinogenic alcamines and their NN-dialkyl derivatives. C. C. CHRISTMAN and P. A. LEVENE (J. Biol. Chem., 1938, 124, 453—458; cf. A., 1924, i, 168).—The Me ester of *dl*-leucine is directly reduced in MeOH by H_2 (175°; 3600 lb./in.²; Cu chromite) to *NN*-dimethyl-*dl*-leucinol (hydrochloride, m.p. 103—104°; picrate, m.p. 105—106°; methiodide). The reduction is also effected in dioxan. *N*-Acetyl-*l*-norleucine Et ester is similarly reduced in MeOH to *NN*-dimethyl-*dl*-norleucinol, b.p. 115° (bath)/15 mm. (picrate, m.p. 89—90°), also obtained from *l*-norleucine Et ester. E. W. W.

Mechanism of trans-amination of amino-acids. F. KNOOP and C. MARTIUS (Z. physiol. Chem., 1938, 254, I—II; cf. Braunstein and Kritzman, A., 1937, II, 448).— AcCO_2H , shaken with arginine in H_2 in presence of a catalyst, gives octopine. The mechanism of the reaction is probably the same as in the interaction of glutamic acid and AcCO_2H .

W. McC.

Action of acetylating agents on amino-acids. A. NEUBERGER (Biochem. J., 1938, 32, 1452—1456).—*dl*-Phenylalanine can be acetylated (Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 2°) without any ketone formation. Acetylation of *l*-histidine in the same way yields a compound (80%), m.p. 155° (indef.), which is partly racemised. Treatment of *l*-proline with keten yields 80% of *N*-acetyl-*l*-proline, whilst *l*-cysteine hydrochloride similarly yields *NS*-diacetylcysteine (50%), m.p. 111—112°, Et *dl*- β -hydroxyglutamate hydrochloride the corresponding *N*-Ac compound (53%), m.p. 46°, and α -thiolpropionic acid an *S*-Ac compound, b.p. 133°/1 mm. P. G. M.

New compounds from sugars and amino-acids. B. HELFERICH and R. MITTAG (Ber., 1938, 71, [B], 1585—1590).—Benzylideneglucofuranose 6-methanesulphonate (I) is transformed by anhyd. NaI in boiling CMe_3 into 3:5-benzylidene-1:2-isopropylideneglucose 6-iodohydrin, m.p. 140° (corr.), $[\alpha]_D^{25} + 20.9^\circ$ in CHCl_3 , which is slowly converted by liquid NH_3 at room temp. into 3:5-benzylidene-1:2-isopropylidene- Δ^5 -glucofuranose-ene (II), m.p. 126° (corr.), $[\alpha]_D^{25} + 66.6^\circ$ in CHCl_3 . Under similar con-



dition (I) is slowly transformed into 6-amino-3:5-benzylidene-1:2-isopropylideneglucose, m.p. 127° N** (A., II.)

(corr.), $[\alpha]_D^{25} + 25.4^\circ$ in CHCl_3 . Gradual addition of 1:2-isopropylidene-5:6-anhydroglucofuranose to alanine Et ester gives the non-cryst. Et α -1:2-isopropylidene-6-glucofuranosylaminopropionate (III), hydrolysed by aq. $\text{Ba}(\text{OH})_2$ at room temp. to 6-N-dl(?)alanino-1:2-isopropylideneglucosylfuranose (III), decomp. about 230°, $[\alpha]_D^{25} - 13.8^\circ$ in H_2O , which is acid towards litmus, dissolves BaCO_3 when heated, and reduces Fehling's solution only after hydrolysis. 6-N-l(+)-Alanino-1:2-isopropylideneglucosylfuranose, decomp. about 210—220°, $[\alpha]_D^{25} - 20.8^\circ$ in H_2O , is obtained similarly. Hydrolysis of (IV) with 35% AcOH affords 6-N-dl(?)alaninoglucose, m.p. indef. about 130—135° (decomp.), $[\alpha]_D^{25} + 48.3^\circ$ in H_2O , which reduces hot Fehling's solution and gives a phenylosazone, m.p. 240° (block.; decomp.) after becoming discoloured at about 225°. 6-N-l-Alaninoglucose, $[\alpha]_D^{25} + 57.2^\circ$ in H_2O , and its phenylosazone, m.p. 252° (decomp.) after becoming discoloured at about 240°, are described. H. W.

Carbamic esters from carbamide. R. A. JACOBSON (J. Amer. Chem. Soc., 1938, 60, 1742—1744).—At the b.p. or 175—190° (whichever is the lower) $\text{CO}(\text{NH}_2)_2$ and ROH give *n*-dodecyl, new m.p. 81—82°, *n*-octyl, m.p. 67°, b.p. 136°/4 mm., and Bu^t carbamate, b.p. 117°/25 mm., m.p. 65—66°, formed also with Bu^t allophanate, new m.p. 174°, from $\text{CO}(\text{NH}_2)_2$, Bu^tOH , *o*- $\text{C}_6\text{H}_4(\text{OBu}^t)_2$, and glycerol at 123—170°. $(\text{CH}_2\cdot\text{OH})_2$ and sorbitol give syrups. $\text{CH}_2(\text{CH}_2\cdot\text{OH})_2$ gives a mixture, including a little of the diurethane, m.p. 108°. The reaction, $\text{CO}(\text{NH}_2)_2 + 2\text{ROH} \rightarrow \text{R}_2\text{CO}_3 + 2\text{NH}_3$, could not be realised; in the presence of H_2SO_4 , $\text{C}_{10}\text{H}_{21}\cdot\text{OH}$ gives quantitatively $(\text{C}_{10}\text{H}_{21})_2\text{O}$. R. S. C.

Condensation of α -keto-acids and acetamide. D. SHEMIN and R. M. HERBST (J. Amer. Chem. Soc., 1938, 60, 1954—1957).— $\text{CO}_2\text{H} \cdot [\text{CH}_2]_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$ (I) and NH_2Ac at 70—75°/10—15 mm. give the lactone (II), m.p. 196°, of α -acetamido- α -hydroxyglutaric acid, converted by *N*-HCl into (I) and by EtOH into an unsaturated ester, which, when hydrogenated (Pt) and hydrolysed, gives glutamic acid. At 110° \pm 5°/10—15 mm. (I) and NH_2Ac give by double condensation and loss of CO_2 $\gamma\gamma$ -diacetamidobutyric acid, m.p. 197°, obtained similarly from (I). At 110—115°/10—15 mm. $\text{CH}_2\cdot\text{C}(\text{NHAc})\cdot\text{CO}_2\text{H}$ and NH_2Ac give $(\text{NHAc})_2\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. $\text{CHPh}\cdot\text{C}(\text{NHAc})\cdot\text{CO}_2\text{H}$ (III) does not react with NH_2Ac , and $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ gives only (III). BzCO_2H gives $\alpha\alpha$ -diacetamidophenylacetic acid, $+\text{H}_2\text{O}$, m.p. 201—202° (decomp.) (uncorr.), with small amounts of $\text{NHBz}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ (IV) and $\alpha\alpha$ -diacetamidotoluene, m.p. 250° (decomp.; uncorr.). $\text{NHAc}\cdot\text{CR}(\text{OH})\cdot\text{CO}_2\text{H}$ is a possible intermediate. The mechanism of the formation of (IV) is discussed. R. S. C.

Synthesis of dipeptides from α -keto-acids. D. SHEMIN and R. M. HERBST (J. Amer. Chem. Soc., 1938, 60, 1951—1954).—Oximes of pyruv-amido-acids or -esters are hydrogenated (PtO_2) in EtOH or aq. EtOH (for some esters addition of a little HCl is advantageous) at 2—3 atm. to yield dipeptides. Pyruvylglycineoxime, m.p. 202° (decomp.), and the Et ester thereof, m.p. 127°, carbethoxyalanylglycine Et ester, new m.p. 72.5—73.5°

α' -diacetamidopropionylalanine, m.p. 175—176° (decomp.), pyruvylalanine, m.p. 143.5° [oxime, m.p. 186°; Et ester, an oil (oxime, an oil)], and carbethoxyalanylalanine Et ester, m.p. 71—72°, are described. Pyruvylphenylalanineoxime, m.p. 187—188°, gives anomalously alanylcyclohexylalanine; hydrolysed to cyclohexylalanine (Bz derivative, m.p. 186—187°). The lactone of α -acetamido- α -hydroxyglutaric acid with Ac_2O gives the oily azlactone lactone, converted by glycine and NaOH into the lactone, m.p. 210° (decomp.), of α' -acetamido- α' -hydroxyglutarylglutamine, $\text{CO}-\text{O}-\text{C}(\text{NHAc})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. R. S. C.

Glutamic acid. E. BARTOW (Congr. int. Quim. pura apl., 1934, 9, V, 181—185; Chem. Zentr., 1936, ii, 2446).—The prep. of glutamic acid from cereal gluten or from molasses residues of beet sugar manufacture (yield, 0—8.8% of dry wt.) is improved by heating with 2N-HCl in a special autoclave.

A. H. C.

Preparation of *d*- and *l*-alanyl-*l*-histidine; their effect on the blood pressure in comparison with *l*-carnosine. M. HUNT and V. DU VIGNEAUD (J. Biol. Chem., 1938, 124, 699—707).—Carbobenzoyloxy-*l*(+)-alanine is treated with PCl_5 and anhyd. Et_2O at 0° and, after removal of part of the solvent, with histidine Me ester in well-cooled CHCl_3 , thus giving carbobenzoyloxy-*l*(+)-alanyl-*l*(-)-histidine (+2H₂O), m.p. 131° (corr.), transformed (H_2 -Pd-black in 4N-H₂SO₄) into *l*(+)-alanyl-*l*(-)-histidine (I), m.p. 157° (corr.), $[\alpha]_D^{25} + 27.0^\circ$ in H₂O, which could not be freed completely from EtOH and H₂O without decomp.; the sulphate, m.p. 183° (corr.), $[\alpha]_D^{25} + 14.1^\circ$ in H₂O, and the salt, C₉H₁₄O₃N₄·CuO, are described. Non-cryst. carbobenzoyloxy-*d*(-)-alanyl-*l*(-)-histidine is transformed into *d*(-)-alanyl-*l*(-)-histidine (II), m.p. 163° (corr.), $[\alpha]_D^{25} + 7.0^\circ$ in H₂O (sulphate, m.p. 215°, $[\alpha]_D^{25} - 2.5^\circ \pm 0.5^\circ$ in H₂O; Cu salt). The prep. of the dipeptides from carbobenzoyloxy-*dl*-alanine is described. (II) is obtained also from *d*(-)-alanine cyclic carboxylic anhydride. Neither (I) nor (II) in 20 times the dose of *l*-carnosine showed any lowering of the blood pressure of cats under amylal anaesthesia. H. W.

Determination of reduced glutathione. A. B. CORKILL and J. F. NELSON (Austral. J. Exp. Biol., 1938, 16, 133—135).—Mason's method (A., 1930, 803) was followed, but a Zeiss Pulfrich photometer was used. D. M. N.

Synthesis of cyanamide by the action of silver oxide on formaldehyde and ammonia. R. FOSSE, R. DE LARAMBERGUE, and J. GAIDON (Compt. rend., 1938, 207, 12—13; cf. A., 1936, 597; 1937, II, 329).—A mixture of equal vols. of 0.1N-CH₂O, N-NH₃, 2N-AgNO₃, and 2N-KOH at 0—5° affords CN·NH₂, isolated as the Ag derivative, in 1.01—3.75% yield. J. L. D.

Preparation of fully acetylated amides of aldonic acids. G. B. ROBBINS and F. W. UPSON (J. Amer. Chem. Soc., 1938, 60, 1788—1789).—Aldonolactones are converted by liquid NH₃ into the amides, which with Ac_2O -ZnCl₂ give Ac₅ and with Ac_2O -H₂SO₄ at 0° give Ac₆ derivatives. Thus

are obtained penta-, m.p. 184—185°, $[\alpha]_D^{25} + 23.6^\circ$, and hexa-acetyl-*d*-gluconamide, m.p. 110°, $[\alpha]_D^{25} + 25.8^\circ$; penta-, m.p. 165—166°, $[\alpha]_D^{25} + 26.7^\circ$, and hexa-acetyl-*d*-galactonamide, m.p. 149.5—150°, $[\alpha]_D^{25} + 19^\circ$; penta-acetyl-*d*-mannonamide, m.p. 110°, $[\alpha]_D^{25} + 38.7^\circ$, and -*d*-gulonamide, m.p. 162—164°, $[\alpha]_D^{25} + 22.7^\circ$. $[\alpha]$ are in CHCl₃. R. S. C.

Condensation products of carbamide with different aldehydes. F. VASS (Brit. Plast., 1938, 10, 115—118).—CO(NH₂)₂ (I) (2 mols.) and 40% CH₂O (1 mol.) in presence of 1% AcOH give methylenebiscarbamide, sol. in EtOH, and methylenecarbamide, insol. in EtOH. (I) (2 mols.) and CH₂O (3 mols.) with HCO₂H or CH₂Cl·CO₂H (3 min.) or AcOH (10—20 min.) or when heated alone, give methylenebis(methylenecarbamide), CH₂(NH·CO·N·CH₂)₂. More dil. solutions give similar products, no intermediates being obtained. The products are colourless and polymerise when kept. Hydrolysis by CH₂Cl·CO₂H or H₂SO₄ gives indefinite products (14.48—33.85% of N). (I) (2 mols.) and MeCHO (3 mols.; as 40% solution) alone or with 1% of AcOH give ethylidene-carbamide, colourless; 1% NH₃ gives only an aldehyde resin. The 2:1 vanillin-(I), 1:1 piperonal-(I), and 1:1 furfuraldehyde-(I) products are obtained as nearly colourless powders; products with other ratios of reactants could not be isolated. R. S. C.

Molecular compounds of carbamide and its derivatives with pharmaceutical compounds. F. ADAMANIS (Kron. farmac., 1936, 35, 93—97, 110—114, 129—135, 154—155, 169—172; Chem. Zentr., 1936, ii, 2405).—The following mol. compounds were obtained: Veronal (I): carbamide (II) (1:1), transition point 145.5°; (I): NH₂·CO·NHPh (III) (1:2), m.p. 231°; (I) and NH₂·CO·NMe₂ (IV) form no compound. (I) and CO(NHMe)₂ (V) form no compound. (I): NH₂Ac (VI) (1:2). NH₂·CO·CO₂Et (VII) and (III), (VII) and (IV), and (VII) and (VI) give only eutectics. NHPh·CO·CO₂Et (VIII) and (II), (VIII) and (IV), (VIII) and (V), and (VIII) and (I) do not give compounds. Resorcinol (IX): (III) (1:1), m.p. 109.2°. (IX): (IV) (1:1), m.p. 68.0°. (IX): (V) (1:1), m.p. 68.2°. Pyrogallol (X): (II) (3:2), m.p. 68.2°. (IX): (I) (1:1), transition point, 99.7°. *o*-, *m*-, and *p*-C₆H₄(OH)₂ do not give compounds with (I). Compounds are not formed from (XIII) and (IV), *o*-OH·C₆H₄·CO₂H or (XIII) and (I). It is concluded that both NH₂ groups of (II) are active and that (I) forms additive compounds with (a) basic compounds through the H of the NH groups, (b) acidic compounds through the N atoms. Deviations from Kordes' results (A., 1927, 1132; 1931, 310) are noted and the probable non-existence of ternary compounds is discussed. A. H. C.

Guanidine structure and hypoglycæmia: sulphur-containing diguanidines. C. E. BRAUN and B. J. LUDWIG (J. Org. Chem., 1938, 3, 16—25).— $\beta\beta'$ -Dithiobis-(α -guanidopropionic acid) (cf. Kapfhammer *et al.*, A., 1934, 876) is converted into its dihydrochloride (I), decomp. 146°, when treated with dry HCl in EtOH or MeOH, or when a solution in dil. HCl is evaporated to dryness in vac. at room temp., the dihydrochloride (II) (A., 1935, 850) of 5:5'- (dithiodimethylene)diglycocyanidine (III) being also

formed. When treated with $3N\text{-NH}_3\text{-H}_2\text{O}$, (I), like (II), gives (III). The guanidine groups of (I) and (II) in H_2O liberate N_2 with HNO_3 , and the results of the determination of $\text{NH}_2\text{-N}$ by Van Slyke's method on freshly prepared solutions of (I) and (II) accord with the view that these are in equilibrium in aq. solution. 4:4'-Dithioaniline dihydrochloride when refluxed (steam-bath, 18 hr.) with CN-NH_2 in EtOH and then treated with cold 10% NaOH gives 4:4'-diguanidodiphenyl disulphide (IV), m.p. 178° (picrate, m.p. 199° ; sulphate, m.p. $257\text{--}258^\circ$, turning into a yellow form of the same m.p. on storage). Similarly $(p\text{-NH}_2\text{-C}_6\text{H}_4)_2\text{S}$ yields 4:4'-diguanidodiphenyl sulphide (V), m.p. $203\text{--}204^\circ$ (decomp.) (sulphate, m.p. $>290^\circ$, which did not turn yellow on storage; picrate, m.p. 168°). No hypoglycemia followed administration of (I), (IV), or (V) in doses up to 100 mg. per kg. of body-wt. and there was no evidence of acute toxicity. The mere presence of $\text{-S}_2\text{-}$ and guanidine residues in a mol. does not give rise to hypoglycemic activity.

H. G. M.

Aliphatic azoxy-compounds. III. β -Azoxy- β -dimethylhexane. J. G. ASTON and D. E. AILMAN. **IV. Preparation of α -azoxy-ketones. Molecular refractions and parachors of aliphatic azoxy-compounds.** D. E. AILMAN (J. Amer. Chem. Soc., 1938, 60, 1930—1933, 1933—1935; cf. A., 1934, 868).—III. β -Nitroso- β -dimethyl-*n*-hexane (I) with $\text{SnCl}_2\text{-HCl}$ or HCl alone at room temp. gives only the decomp. products of (I), viz., N_2 , a little N_2O , $\text{iso-C}_5\text{H}_{11}\cdot\text{CMe}_2\cdot\text{OH}$ (II), $\text{iso-C}_5\text{H}_{11}\cdot\text{CMe}_2\text{Cl}$ (III), and octanes; with $\text{SnCl}_2\text{-HCl}$ at $57\text{--}60^\circ$ β -amino- β -dimethylhexane, b.p. $94^\circ/150$ mm. (hydrochloride, m.p. 171°), is obtained. As (I) dissociates at 55° into the unimol. form, it is only this form which is reduced to the amine, and the bimol. form contains a N-N linking. $\text{iso-C}_5\text{H}_{11}\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{OH}$, (I), and $\text{K}_2\text{CO}_3\text{-KOH}$ at 50° give 75% of β -azoxy- β -dimethylhexane (IV), b.p. $111^\circ/5$ mm., obtained also in 9.5% yield from the amine and NO_2 -compound. $\text{SnCl}_2\text{-HCl}$ merely hydrolyses (IV) to N_2 , octenes, (II), and (III); SnCl_2 alone, but not HCl or SnCl_4 , gives the same products. (IV) reacts very slowly with MgMeI , which is evidence against an open-chain structure for aliphatic azoxy-compounds.

IV. The parachor and $[n]$ of (IV), *Et* α -azoxy-isopropyl, b.p. $126\text{--}126.5^\circ/6$ mm., and -isobutyl ketone, m.p. $30\text{--}31^\circ$ (prep. from the NO -compounds by $\text{SnCl}_2\text{-HCl}$), give const. vals. for the N_2O group, but afford no evidence in favour of an open-chain structure.

R. S. C.

Synthetic mannose- and galactose-1-phosphoric acid. S. P. COLOWICK (J. Biol. Chem., 1938, 124, 557—558; cf. A., 1938, II, 39).—Acetobromogalactose (A., 1929, 682) and Ag_3PO_4 in C_6H_6 give tris(tetra-acetyl-galactose-1)-phosphoric acid, $[\alpha]_D^{25} + 118^\circ$ in MeOH, hydrolysed (0.2N-HCl in 96% MeOH at 25°) to galactose-1-phosphoric acid, $[\alpha]_D^{25} + 143^\circ$ [Ba salt (+3H₂O), $[\alpha]_D^{25} + 91^\circ$ in H₂O]. Similarly tris(tetra-acetylmannose-1)-phosphoric acid, $[\alpha]_D^{25} + 31.8^\circ$ in MeOH, and mannose-1-phosphoric acid, $[\alpha]_D^{25} + 58^\circ$ [Ba salt (+3H₂O), $[\alpha]_D^{25} + 36^\circ$ in H₂O], are prepared.

E. W. W.

Phosphorylation of glycogen *in vitro*. W. Z. HASSID and I. L. CHAIKOFF (Science, 1938, 88, 15—16).—Details of the prep. of the Ca salt of the phosphoric ester of glycogen from glycogen, CaCO_3 , and POCl_3 are given. The final H_2O -sol. product, $[\alpha]_D^{25} + 174^\circ$, contained P 1.73 and Ca 2.66%, but gave no test for PO_4''' until it had been treated with H_2O_2 and conc. HNO_3 containing a trace of $\text{Fe}(\text{NO}_3)_3$.

L. S. T.

"Phosphatatic" action of hydrogels. I. Fission of esters of phosphoric acid in the presence of lanthanum hydroxide. E. BAMANN and M. MEISENHEIMER (Ber., 1937, 71, [B], 1711—1720).—Solutions of Na β -glycerophosphate (I) are mixed with $\text{NH}_4\text{Cl-NH}_3$ at 37° and LaCl_3 is added; after definite intervals the H_3PO_4 liberated is determined colorimetrically. Hydrolysis occurs best at p_H 7.5—8.0. Generally, the process does not long continue in accordance with the initial rate; at p_H 9.5 the graph is linear until the change is about 30% complete but in less strongly alkaline solution the rate declines considerably sooner. Reaction is similar in presence of a veronal-NaOAc buffer but its extent is greater. The rate of hydrolysis increases with the concn. of the ester solution. Gels formed in the reaction mixture containing the substrate do not suffer appreciable loss of activity when rendered compact by being centrifuged or when washed with buffer solution. The substrate appears to protect the active parts of the surface, probably by the formation of a $\text{La}(\text{OH})_3$ -phosphate compound. Gels pptd. in the buffer mixture in the absence of substrate suffer considerable loss of activity when washed with a suitable medium; their initial low activity becomes improved as the experiment progresses. During the course of the hydrolysis the gel sometimes passes into an unstable sol from which a new gel is derived; the phenomenon depends on the p_H of the medium and the concn. of the substrate. The behaviour of phenyl- and diphenyl-phosphoric acid is similar to that of (I) whereas hexosediphosphoric acid (Ca or K salt) and inositolhexaphosphoric acid (Ca-Mg compound or Na salt) are less readily hydrolysed.

H. W.

Alkyl- and aryl-substituted esters of orthosilicic acid. I. Preparation of magnesium organic compounds without the use of ethyl ether, in presence of ethyl silicate. II. Synthesis of alkyl-substituted ethyl esters of silicic acid. K. ANDRIANOV and O. GRIBANOVA (J. Gen. Chem. Russ., 1938, 8, 552—557, 558—562).—I. The reaction $\text{RX} + \text{Mg} \rightarrow \text{MgRX}$ ($\text{R} = \text{Et}, \text{Bu}^\beta, \text{isoamyl}, \text{CHMeBu}^\alpha, \text{sec-octyl}, \text{Ph}$; $\text{X} = \text{Cl}, \text{Br}$) takes place in presence of $\text{Si}(\text{OEt})_4$, with or without solvent.

II. The reactions $\text{RMgX} + \text{Si}(\text{OEt})_4 \rightarrow \text{RSi}(\text{OEt})_3 + \text{MgX}\cdot\text{OEt} \leftarrow \text{Mg} + \text{RX} + \text{Si}(\text{OEt})_4$ are described ($\text{X} = \text{Cl}, \text{Br}$). The compounds $\text{SiR}(\text{OEt})_3$ ($\text{R} = \text{Et}, \text{R} = \text{Pr}^\beta, \text{R} = \text{Bu}^\beta$, b.p. $180\text{--}195^\circ$, $\text{R} = \text{isoamyl}$, $\text{R} = \text{hexyl}$, b.p. $200\text{--}220^\circ$) are described.

R. T.

Decomposition of mercury dimethyl.—See A., 1938, 1, 466.

Mercury derivatives of symmetrical dichloroethylene. M. FITZGIBBON (J.C.S., 1938, 1218—1222).—*cis*- $\text{CHCl}\cdot\text{CHCl}$ with $\text{Hg}(\text{CN})_2\text{-NaOH-H}_2\text{O}$ gives Hg bischloroacetylide, $[(\text{CCl}\cdot\text{C})_2\text{Hg}]$ (I), which

explodes at 174—175° (cf. Hofmann *et al.*, A., 1910, i, 16) and with conc. HCl gives spontaneously inflammable CH:CCl. When this CH:CCl oxidises slowly, considerable quantities of O₃ are formed; the formation of an unstable ozonide may account for the explosive nature of crude (I). When pure, (I) is stable, but it slowly decomposes when kept under EtOH. *trans*-CHCl:CHCl with Hg(CN)₂-NaOH-H₂O gives Hg bisdichloroethylenide, [(CHCl:CCl)₂Hg] (II), m.p. 50.3°, together with more complex derivatives, m.p. < 185°, considered to be chain compounds, CHCl:CCl-[Hg:CCl:CCl]_n-H; *n* is probably 2 and 3, respectively, for the product less sol. than (II) in Et₂O, and the insol. residue. When heated with HgCl₂ in EtOH and the product steam-distilled, (II) gives chloromercury dichloroethylenide (III), m.p. 80.6°, which with KI gives the corresponding iodide, CHCl:CCl·HgI, m.p. 115° (decomp. 125°), which cannot be recrystallised owing to decomp. into I and HgI₂. With conc. HCl both (II) and (III) give C₂H₂Cl₂ and HgCl₂, and with hot Na₂S-H₂O, HgS is formed. Strong bases convert (III) into an insol. white amorphous substance. Better yields of (II) and of Hg bistrichloroethylenide (from C₂HCl₃) are obtained when the NaOH-H₂O is replaced by NaOEt-EtOH. H. G. M.

Lead organic complexes. M. LESBRE (Compt. rend., 1938, 206, 1481—1483).—PbMeCl₂ (cf. A., 1937, II, 372) with excess of quinoline hydrochloride in presence of HCl affords PbMeCl₂·2C₉H₇N, hydrolysed to methylplumbonic acid (A., 1935, 611). The tribromide gives easily decomposable complexes. PbEtI₃ with C₅H₅N similarly affords PbEtI₃·2C₅H₅N which decomposes at room temp. with liberation of I. No acids of the type (PbRX₃)₂ or their alkali salts are isolable (cf. A., 1935, 966). Boiling aq. PbCl₂ with *o*-OH·C₆H₄·CO₂H in EtOH affords a complex (Pb^{IV}) which partly sublimes above 80° and dissociates strongly in concns. < 0.02N. 0.001N solutions form a basic Pb salicylate. No complex oxalate of the type described by Reis (A., 1881, 843) can be isolated. J. L. D.

Stereoisomeric forms of 1:2-diphenylcyclopentane. H. A. WEIDLICH (Ber., 1938, 71, [B], 1601—1603; cf. Bernhauer and Hoffmann, A., 1937, II, 498).—Treatment of Me₃ *meso*-βγ-diphenyladipate with finely-divided Na in boiling C₆H₆ gives *cis*-3:4-diphenylcyclopentanone, b.p. 115°/0.02 mm., m.p. 107°, reduced (Clemmensen) to *cis*-1:2-diphenylcyclopentane (I), m.p. 47°. Analogously, Me *r*-βγ-diphenyladipate gives *trans*-3:4-diphenylcyclopentanone (II), b.p. 180°/0.02 mm., m.p. 177°, whence *trans*-1:2-diphenylcyclopentane, m.p. 65°. Von Liebig's observation (A., 1914, i, 845) of the reduction of (II) to (I) appears erroneous. H. W.

Monohalogeno-derivatives of methylcyclohexane. M. MOUSSERON and R. GRANGER (Compt. rend., 1938, 206, 1486—1488).—1-Methylcyclohexanol (I) with HCl at 100° or PCl₅ in C₆H₆ at 0° affords only 1-chloro-1-methylcyclohexane (II), the Mg derivative of which is oxidised to (I) or converted into 1-methylcyclohexane-1-carboxylic acid, m.p. 39° (amide, m.p. 68°). *trans*-2-Methylcyclohexanol with HCl affords

(II), *trans*- and *cis*-1-chloro-2-methylcyclohexane, converted as above into the *cis*-1-carboxylic acid (anilide, m.p. 106°) and the *cis*-1-OH-compound (*Ph* carbamate, m.p. 94°) which with PCl₅ affords a mixture of isomeric Cl-compounds, the *trans*-isomeride predominating (corresponding anilide and *Ph* carbamate, m.p. 152° and 105°, respectively). *dl-trans*-3-Methylcyclohexanol with HCl affords 1-methyl-Δ³-cyclohexene (III) and a mixture of Cl-compounds containing 60% of *cis*-1-chloro-3-methylcyclohexane (IV), b.p. 40°/10 mm., converted as above into the 1-hydroxy- (*Ph* carbamate, m.p. 90°) and 1-carboxy- (V) (anilide, m.p. 102—103°)-compounds. (IV) with PCl₅ affords some (III) but mainly the *trans*-isomeride, b.p. 39°/10 mm., of (IV) (*Ph* carbamate and anilide corresponding with those from the *cis*-form have m.p. 93° and 110—111°, respectively). The Me esters of (V) and its *trans*-analogue when fractionally distilled are separated into *d*- and *l*-forms. *trans*-4-Methylcyclohexanol with HCl affords (III) (20%), *cis*- and *trans*-1-chloro-4-methylcyclohexane. As above, the former is converted into a 1-carboxylic acid (anilide, m.p. 149—150°) and a 1-OH-compound (*Ph* carbamate, m.p. 118—119°) which with PCl₅ affords the *trans*-isomeride (corresponding anilide and *Ph* carbamate have m.p. 108—109° and 124—125°, respectively). *cis*- or *trans*-3-Methylcyclohexanol (VI) with HBr affords (III) and *cis*-1-bromo-3-methylcyclohexane, b.p. 59°/10 mm., converted into *cis*-(VI) (*p*-nitrobenzoate, m.p. 78—79°). *cis*- or *trans*-(VI) with PBr₅ affords *trans*-1-bromo-3-methylcyclohexane, b.p. 58°/10 mm., which rapidly loses HBr. *trans*-(VI) with HI affords *cis*-1-iodo-3-methylcyclohexane, b.p. 72°/10 mm. J. L. D.

Reduction of potassium permanganate by cyclic hydrocarbons.—See A., 1938, I, 463.

Free radicals containing a cyclohexane ring. I. Diphenyl-*p*-cyclohexylphenylmethyl. I. ZUGRAVESCU and S. ZUGRAVESCU (Bul. Soc. Chim. România, 1937, 19, 85—92).—Me *p*-cyclohexylbenzoate with MgPhBr (2 mols.) in Et₂O gives diphenyl-*p*-cyclohexylphenylcarbinol, b.p. 100°/2 mm., converted by AcCl in C₆H₆ into diphenyl-*p*-cyclohexylphenylmethyl chloride (I), m.p. 123°, which in dry C₆H₆ with Cu powder (CO₂ atm.) gives a red colour, due to diphenylcyclohexylphenylmethyl, and yields *s*-tetraphenyldicyclohexylphenylethane (an oil). Oxidation of (I) by air in C₆H₆ with Cu powder yields the peroxide, m.p. 164°. J. D. R.

Isomerisation of carotenoids. L. ZECHMEISTER and P. TUZSON [with, in part, I. BERGER] (Biochem. Z., 1938, 32, 1305—1311).—Solutions of chromatographically pure lycopene, β-carotene, or cryptoxanthin undergo, when kept at room temp., a partial isomerisation which manifests itself in the decrease of the colorimetric val. and in the displacement of the absorption max. towards shorter λ. The rate of this spontaneous isomerisation, which tends towards an equilibrium, increases on heating. The interconversion is reversible. Partly isomerised solutions always give two distinct layers in the Tswett column; the phenomenon is not caused by the adsorption experiment itself but is already present in the solution. H. W.

Raman effect in diagnosis of the constituents of a mixture of isomeric dihalogenated benzene derivatives. R. PAJEAU (Compt. rend., 1938, 207, 344—345).—On bromination in presence of BeBr_2 , C_6H_6 gives small quantities of *o*- and *p*- $\text{C}_6\text{H}_4\text{Br}_2$, and PhCl gives *o*- and *p*- $\text{C}_6\text{H}_4\text{ClBr}$. In presence of AlCl_3 , PhCl gives all three isomerides. A. J. E. W.

By-products in aromatic nitration. G. M. BENNETT and P. V. YOULE (Nature, 1938, 142, 356).—OH by-products are formed in considerable amounts in the nitration of aromatic compounds with *m*-directing groups; e.g., nitration of PhNO_2 gives 0.5—6.5% of styphnic acid. The mechanism of the process is discussed. L. S. T.

Reaction of double decomposition. G. K. HAÜSER (Mem. Inst. Chem. Tech. Ukrain. Acad. Sci., 1938, No. 7, 121—127).—When Na_2CO_3 containing NaHCO_3 is added to aq. *m*- $\text{C}_6\text{H}_4(\text{SO}_3)_2\text{Ca}$ CO_2 is not immediately evolved, owing to the formation of $\text{Ca}(\text{HCO}_3)_2$. R. T.

Separation of sulphuric acid from nitric, alkyl- and aryl-sulphonic, and alkyl sulphuric acids by means of liquid ammonia. J. H. BILLMAN and L. F. AUDRIETH (J. Amer. Chem. Soc., 1938, 60, 1945—1946).—Since $(\text{NH}_4)_2\text{SO}_4$ is insol. in liquid NH_3 , H_2SO_4 can be separated from HNO_3 , RSO_3H , ArSO_3H , or RHSO_4 ($\text{R} = \text{alkyl}$) by dissolution in liquid NH_3 and filtration. By evaporating the filtrate NH_4 sulphanilate, $+0.5\text{H}_2\text{O}$, benzene-, *o*-amino-benzene-, $+0.5\text{H}_2\text{O}$, *p*-toluene-, 2-aminotoluene-5-, *d*-camphor-, *o*-, *m*-, and *p*-nitrobenzene-, and 2-naphthalene-sulphonate, naphthionate, lauryl sulphate, and Et sulphate are obtained. PhSO_3Na and $\text{Bu}^n\text{SO}_3\text{Na}$ are insol., and $\text{Na}(n\text{-C}_{12}\text{H}_{25})\text{SO}_4$ and $\text{Na}(\text{CH}_2\text{Ph})\text{SO}_4$ slightly sol., in liquid NH_3 . R. S. C.

Sulphonation of cold aromatic hydrocarbons. I. TANASESCU and M. MACAROVICI (Bull. Soc. chim., 1938, [v], 5, 1126—1129).— C_6H_6 is transformed by H_2SO_4 (d 1.84) at 22° during 24 hr. into PhSO_3H , m.p. 52—53°, the bulk of which remains in the acid layer. The yield depends on the quality of C_6H_6 and H_2SO_4 . Less satisfactory yields are obtained from pure C_6H_6 , free from thiophene, and H_2SO_4 with 7% of added SO_3 . Under the same conditions, PhCl gives exclusively *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_3\text{H}$, m.p. 92—93° (lit. m.p. 68°), PhBr gives *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_3\text{H}$, m.p. 88—90°, and PhMe yields solely *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$, m.p. 103—104°, free from sulphone. H. W.

Catalytic effects in the bromination of toluene. M. S. KHARASH, P. C. WHITE, and F. R. MAYO (J. Org. Chem., 1938, 3, 33—47).—The mechanism proposed for the formation of CH_2PhBr in the bromination of PhMe consists in a chain reaction initiated by Br atoms, and is in accord with previous work which is reviewed. Nuclear substitution, probably a bimol. reaction, increases in rate with increasing $[\text{Br}]$, but does not involve Br atoms. The *ortho*-*para* ratio is unaffected by the presence of peroxides, but the yield of CH_2PhBr is greatly increased by addition of org. peroxides (Bz_2O_2 , ascaridole, triacetone peroxide) to dil., but not conc., solutions of Br in PhMe in reactions in the dark in presence of air. In photobromination, the rate of reaction and the yield of CH_2PhBr are

reduced, and the yield of $\text{C}_6\text{H}_4\text{MeBr}$ is increased, by exclusion of O_2 , presence of which, it is suggested, may be essential to this reaction. Side-chain substitution in photobromination and in the peroxide-catalysed reaction is completely inhibited by small amounts of NO-compounds. AcOH and PhNO_2 , as solvents, inhibit the latter reaction, but increase the rate of nuclear substitution. CCl_4 acts as an inert diluent. Side-chain bromination of PhEt is greatly increased, in the dark, by addition of peroxides. These results support the proposed mechanism, and accord with the view that Br atoms may also be liberated from HBr by light in presence of O_2 and peroxides (cf. A., 1937, II, 373). H. G. M.

Catalysed polymerisation of styrene. II.—See A., 1938, I, 464.

Isomerisation of isostilbene to stilbene by hydrogen bromide in presence of oxygen and of ferromagnetic metals. Y. URUSHIBARA and O. SIMAMURA (Bull. Chem. Soc. Japan, 1938, 13, 566—569; cf. A., 1938, II, 48; Kharasch *et al.*, A., 1937, II, 332).—The change isostilbene \rightarrow stilbene in presence of HBr in the dark is accelerated by O_2 in C_6H_6 , by reduced Ni or Fe (no solvent), much less by Pt-black, Pd-black, or Cu, and not at all by Ni in C_6H_6 . *o*- $\text{C}_6\text{H}_4(\text{OH})_2$ inhibits the action of HBr in sunlight, and of HBr and Ni, HBr and O_2 , or HBr at 100°, in the dark. NHPh_2 inhibits slightly the action of HBr and O_2 in the dark, but has no effect on the others. A. Li.

Synthesis of disubstituted acetylenes. J. R. JOHNSON, A. M. SCHWARTZ, and T. L. JACOBS (J. Amer. Chem. Soc., 1938, 60, 1882—1884).—Disubstituted acetylenes are readily prepared from *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{R}$ and $\text{CR}'\text{:CNa}$ or $\text{CR}'\text{:C}\cdot\text{MgBr}$. Thus CPh:CNa in Bu^n_2O or PhMe gives 77% of CPh:CET , b.p. 82°/5 mm. (hydrated to COPhPr^a), in Bu^n_2O 75% of α -phenyl- β - γ -chloropropylacetylene, b.p. 125—127°/4 mm. (converted by way of the nitrile into the acid, which with KMnO_4 yields BzOH and $\text{CO}_2\text{H}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$), and in PhMe 65—70% of $\text{CPh:C}\text{Bu}^a$, b.p. 109—110°/12 mm. (hydrated to $\text{COPh}\cdot\text{C}_5\text{H}_{11}\cdot\text{n}$). *n*- $\text{C}_8\text{H}_{17}\cdot\text{C:CNa}$ in Bu^n_2O gives 63% of Δ^7 -dodecinene, b.p. 95°/12 mm. (oxidised to EtCO_2H and $\text{C}_8\text{H}_{17}\cdot\text{CO}_2\text{H}$), and 65% of α -chloro- Δ^8 -tridecinene, b.p. 123—124°/3 mm. (converted by way of the nitrile into the acid, which with KMnO_4 gives $\text{CO}_2\text{H}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ and $\text{C}_8\text{H}_{17}\cdot\text{CO}_2\text{H}$). $\text{CPh:C}\cdot\text{MgBr}$ (not CPh:CNa) gives $\text{CPh:C}\cdot\text{CH}_2\text{Ph}$ and 46% of δ -chloro- Δ^a -butinenylbenzene, b.p. 95°/3 mm. R. S. C.

Raman spectra of hydrocarbons containing tertiary C-D linkings. W. G. BROWN, C. J. MIGHTON, and M. SENKUS (J. Org. Chem., 1938, 3, 62—75).—The Raman lines for CHPh_3 (freed from fluorescent material by distillation in vac.), CHPh_2Me , CHPhMe_2 (cf. A., 1937, I, 113), and $\text{CHMe}_2\cdot\text{CH}_2\text{Ph}$, and the corresponding *tert*.-deutero-compounds, triphenyldeuteromethane, m.p. 91—92° (prepared from NaCPh_3 and AcOD : reduction of CPh_3Cl with $\text{Zn}\cdot\text{AcOD}$ is accompanied by substitution of D in the C_6H_6 rings), diphenylmethyldeuteromethane, b.p. 136—137°/12 mm. (prepared from AcOD and KCPh_2Me , obtained from $\text{CPh}_2\text{Me}\cdot\text{OMe}$ and $\text{Na}\cdot\text{K}$), phenyldimethyldeuteromethane, b.p. 150.0° (similarly pre-

pared), and *benzylidimethyldeuteromethane*, b.p. 170.5—171.5° (prepared from $\text{CH}_2\text{Ph}\cdot\text{CMe}_2\cdot\text{MgCl}$ and AcOD). The C—D lines for the last four compounds have frequencies of 2132, 2122, 2152, and 2147 ± 5 cm^{-1} , respectively. It is concluded that the binding force for the *tert.* C—H linking is essentially const. in this series of compounds and comparable with that of the corresponding linking in CHMe_3 , and that the factors responsible for the differences in chemical behaviour exert a negligible influence on the normal states of the mols. The increase in the binding force of the C—H linking in halogen-substituted methanes is attributed primarily to electrostatic attraction between halogen and H. H. G. M.

Reaction between dichlorodiphenylmethane and salts of organic acids as a method of preparation of anhydrides of organic acids. V. V. EVLAMPIEV and N. P. GURIANOV (Utschen. Zap. Univ. Kazan, 1937, 97, No. 8, 55—69).— CPh_2Cl_2 on warming with AgOAc without solvent to 100° or on mixing with AgOAc in light petroleum at room temp. gives COPh_2 and Ac_2O , presumably through the unstable ester $\text{CPh}_2(\text{OAc})_2$. The yield is high. Analogous reactions are also possible with NaOAc , $\text{Pr}^n\text{CO}_2\text{Na}$, NaOBz , $(\text{CH}_2\text{CO}_2\text{Na})_2$, and Na palmitate. CPh_2Cl_2 and HCO_2Na give COPh_2 , HCO_2H , HCl , etc. J. J. B.

Propinene—allene tautomerism. $\alpha\gamma$ -Diphenylpropinene (phenylbenzylacetylene) and related compounds. J. R. JOHNSON, T. L. JACOBS, and A. M. SCHWARTZ (J. Amer. Chem. Soc., 1938, 60, 1885—1889).—The prototropic change, $\text{C}:\text{Ar}:\text{C}:\text{CH}_2\text{Ar} \longleftrightarrow \text{CHAr}:\text{C}:\text{CHAr}$, is similar to the changes, $\text{CH}_2\text{R}:\text{CN} \longleftrightarrow \text{CHR}:\text{C}:\text{NH}$, and $\text{CPh}:\text{C}:\text{NH}_2$ (produced by Hofmann degradation of $\text{CPh}:\text{C}:\text{CO}\cdot\text{NH}_2$) $\longrightarrow \text{CHPh}:\text{C}:\text{NH} \longleftrightarrow \text{CH}_2\text{Ph}:\text{CN}$, and analogous to the anionotropic changes, $\text{CR}_2\text{Br}:\text{C}:\text{CR} \longrightarrow \text{CR}_2:\text{C}:\text{CRBr}$ and $\text{OH}:\text{CR}_2:\text{C}:\text{CR} \longrightarrow \text{CR}_2:\text{CH}:\text{COR}$. It does not, however, occur when $\text{Ar} = \text{Ph}$ or $p\text{-C}_6\text{H}_4\text{Br}$, since $\alpha\gamma$ -diphenyl- (I), γ -phenyl- α - p -bromophenyl- (II), and α -phenyl- γ - p -bromophenyl- Δ^a -propinene (III) exist and react only as such. $\text{C}:\text{CPh}$ has thus less activating effect on CH_2 than has CN or $\text{C}:\text{CH}$, a result in line with electronic considerations. $\text{CPh}:\text{C}:\text{MgBr}$ and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{CH}_2\text{Ph}$ (IV) in Et_2O give 72% of (I), b.p. 128—129°/1—2 mm., obtained also in 27% yield from MgPhBr and $\text{CPh}:\text{C}:\text{CH}_2\text{Br}$. With KMnO_4 (I) gives BzOH (48%) and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ (15%), with $\text{HgO}\cdot\text{H}_2\text{SO}_4\cdot\text{EtOH}$ gives 50% of $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COPh}$, and in CCl_4 yields $\alpha\beta$ -dibromo- $\alpha\gamma$ -diphenyl- Δ^a -propene, m.p. 60°, and an oily I_2 -compound. $p\text{-C}_6\text{H}_4\text{Br}:\text{C}:\text{CH}$, b.p. 71—72°/3 mm., m.p. 62—63°, with MgEtBr gives a Grignard reagent, converted by (IV) into (II) (26% yield), m.p. 87°, which with $\text{HgO}\cdot\text{H}_2\text{SO}_4\cdot\text{EtOH}$ gives p -bromo- γ -phenylpropiophenone, m.p. 98—99° (semicarbazone, m.p. 164—165°; oxime, m.p. 115—125°), also obtained from $p\text{-C}_6\text{H}_4\text{Br}:\text{CN}$ and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgBr}$. p -Bromobenzyl p -toluenesulphonate, m.p. 74—75°, and $\text{CPh}:\text{C}:\text{MgBr}$ give 50% of (III), b.p. 166—169°/1—2 mm., m.p. 42—44°, which yields $\alpha\beta$ -dibromo- α -phenyl- γ -bromophenyl- Δ^a -propinene, m.p. 108—108.5, and γ - p' -bromophenylpropiophenone, m.p. 68.5—69° (semicarbazone, m.p. 161—162°; 2:4-dinitrophenylhydrazones, m.p. 67—67.5°), also obtained from $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COCl}$ and ZnPh_2 . R. S. C.

Structure of distyrenes. L. MARION (Canad. J. Res., 1938, 16, B, 213—217).—

$\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ (modified prep. from $\text{CH}_2\text{Bz}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, m.p. 75°, yields (Na-EtOH reduction of the ester) $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{OH}$ (I), b.p. 174—180°/1 mm., dehydrated by KHSO_4 to $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CPh}:\text{CH}_2$ (II), b.p. 140°/2—3 mm., which is oxidised by KMnO_4 to $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COPh}$ (III), isomerises when kept to (? trans)- $\alpha\gamma$ -diphenyl- Δ^a -butene, m.p. 47—47.5°, b.p. 130—140°/1 mm. [dibromide (IV), m.p. 86.5°; with O_3 gives PhCHO and $\text{CHPhMe}\cdot\text{CHO}$]. Dehydration of (I) by hot 20% H_2SO_4 also yields (II), which in this case isomerises to $\alpha\gamma$ -diphenyl- Δ^b -butene, an oil, which gives an unstable dibromide and with KMnO_4 yields (III), BzOH , COPhMe , and (?) $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$. The distyrene obtained by pyrolysis of polystyrene (mol. wt. 8000) contains no (II) (cf. Staudinger *et al.*, A., 1935, 740). $\alpha\gamma$ -Diphenylpropane, b.p. 124°/2 mm. [$(\text{NO}_2)_4$ -derivative, m.p. 169°], is obtained by Clemmensen reduction of $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, into which it is reconverted by CrO_3 in hot AcOH . (IV) is also obtained from (II). M.p. are corr. R. S. C.

Configuration of certain diphenyl compounds indicated by their dipole moments.—See A., 1938, I, 437.

Catalytic condensation of Grignard reagents with hydrocarbons. M. S. KHARASCH, W. GOLDBERG, and F. R. MAYO (J. Amer. Chem. Soc., 1938, 60, 2004).—Formation of Ph_2 derivatives from MgArX and hydrocarbons involves the pre-formed Grignard reagent. Presence of at least catalytic amounts of H_2O and Mg are necessary, which indicates their participation in a chain reaction. Use of a min. amount of Et_2O is essential. The reaction is a general one. $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ with C_6H_6 gives CH_2Ph_2 (29%) and $(\text{CH}_2\text{Ph})_2$ (18%), with m -xylene gives 2:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2\text{Ph}$ (17%), with mesitylene gives 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\text{Ph}$ (20%), but with cyclohexane gives no benzylcyclohexane. MgPhBr with PhMe gives $p\text{-C}_6\text{H}_4\text{PhMe}$ (about 10%) and Ph_2 (20%), with m -xylene gives $\text{C}_6\text{H}_3\text{PhMe}_2$ (9%), with PhCl gives $\text{C}_6\text{H}_4\text{PhCl}$ (9%) and Ph_2 (39%), and with cyclohexane gives Ph_2 (39%) (no phenylcyclohexane). MgMeI and C_6H_6 give only 0.06% of PhMe and 0.03% of p -xylene. R. S. C.

Mechanism of the Fittig reaction. O. BLUMBERGMANN (J. Amer. Chem. Soc., 1938, 60, 1999).—The formation of Ph radicals during the Fittig reaction is confirmed by the reaction of PhBr , C_6H_6 , and Na in N_2 to give Ph_2 , $p\text{-C}_6\text{H}_4\text{Ph}_2$ (I), and $o\text{-C}_6\text{H}_4\text{Ph}\cdot\text{OH}$, and by reaction of NaPh (from HgPh_2 and Na in C_6H_6) with PhBr to give Ph_2 and (I). (I) arises by disproportionation of Ph to C_6H_6 and $\text{C}_6\text{H}_5\cdot$. R. S. C.

Cracking of tetrahydronaphthalene with aluminum chloride. M. B. TUROVA-POLAK and N. B. LUBIMOVA (J. Gen. Chem. Russ., 1938, 8, 538—543).—Tetrahydronaphthalene when distilled at 170—270° from AlCl_3 yields chiefly C_6H_6 and its homologues, together with some cyclopentane and -hexane. R. T.

Dehydration of certain cyclopentanol homologues. II. J. I. DENISENKO (J. Gen. Chem.

Russ., 1938, 8, 410—412).— α -Phenyl- β -1-hydroxy-cyclopentylethane and anhyd. $\text{H}_2\text{C}_2\text{O}_4$ at 130—135° yield 1:2-trimethylene-1:2:3:4-tetrahydronaphthalene, from which 4:5-benzointhane is obtained by passing over C—Pt at 300° in a stream of CO_2 or H_2 .

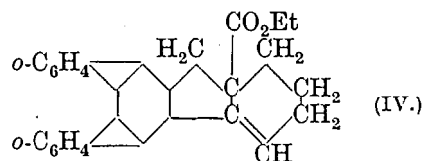
R. T.

1:2:3:4-Dibenzphenanthrene. I. E. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 1798—1799).—Unsuccessful attempts to synthesise 1:2:3:4-dibenzphenanthrene are described. β -9-Phenanthryl-ethylmagnesium bromide and 2-methylcyclohexanone give, with (?) a little 9-ethylphenanthrene, 1-methyl-2-9'-phenanthrylethyl- Δ^1 -cyclohexene, b.p. 220°/0.01 mm. (picrate, m.p. 124—125°; absorbs 2 Br), cyclised by SnCl_4 and HCl in C_6H_6 at room temp. to a spirane, b.p. 220°/0.01 mm. (picrate, m.p. 172°); which with Se at 300—320° gives poor yields of phenanthrene and a hydrocarbon, $\text{C}_{22}\text{H}_{14}$, m.p. 184° (picrate, m.p. 220°). Dicyclohexenyl and 1:2-naphthaquinone at 180° give a resin, but 3-bromo-1:2-naphthaquinone does not react at 100° in $(\text{CHCl}_2)_2$. The K derivative of Et cyclohexanone-2-carboxylate does not react with β -9-phenanthrylethyl chloride. R. S. C.

Magnetochemical investigations of hexa-aryl-ethanes. E. MÜLLER and W. KRUCK (Ber., 1938, 21, [B], 1778—1783).—Preliminary results show that in accordance with quantum-theoretical views the introduction of groups such as the chrysyl and phenanthryl residues which increase the energy of union also increase to a very marked extent the dissociability of hexa-arylated ethanes. The observations are not in themselves a complete verification of the quantum theories. 2-Benzoylchrysene and LiPh in C_6H_6 give diphenyl-2-chrysylcarbinol, m.p. 238°, converted by AcCl in boiling C_6H_6 into diphenyl-2-chrysylmethyl chloride, m.p. 194—195° (slight decomp.), which with Cu powder in C_6H_6 affords $\alpha\alpha\beta\beta$ -tetraphenyldi-2-chrysylethane, m.p. 239° (decomp.) (also $+1\text{C}_6\text{H}_5$); this is dissociated to the extent of at least 65% in C_{10}H_8 at 125°. Diphenyl-9-phenanthrylcarbinol is transformed by AcCl in Et_2O saturated with HCl into diphenyl-9-phenanthrylmethyl chloride, m.p. 178°, converted by Hg in C_6H_6 at room temp. or by Cu powder in boiling C_6H_6 into a dimeric product, $\text{C}_{54}\text{H}_{38}$, m.p. 223—225° under N_2 but varying with the mode of heating. Me phenanthrene-3-carboxylate and LiPh in Et_2O give diphenyl-3-phenanthrylcarbinol, m.p. (crude) 80°, converted by $\text{MeOH}-\text{C}_6\text{H}_6$ or $\text{MeOH}-\text{COMe}_3$ into diphenyl-3-phenanthrylcarbinyl Me ether, m.p. 144—145°. This with AcCl in Et_2O gives diphenyl-3-phenanthrylmethyl chloride, m.p. 129—130°, which with Hg in C_6H_6 gives a dark red solution extremely sensitive to air; the corresponding peroxide has m.p. 195—196°. H. W.

1:2-cyclopentenotriphenylene. II. E. BERGMANN and F. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 1805—1807).—The compounds previously (A., 1936, 1371) considered to be cyclopentenotriphenylene, 7-methyl-1:2-benzopyrene, and 1:2:3:4-dibenzfluorene are shown to be (? 9'-methyl-3:4-benzopyrene (I), 1:2:3:4-dibenzfluorene (II), and cyclopentenotriphenylene (III), respectively. The adduct of 9-cyclopentenylphenanthrene and maleic anhydride with

$\text{Pb}(\text{OAc})_4$, best in $\text{AcOH}-\text{Ac}_2\text{O}$ at 75°, gives 1:2-cyclopentenotriphenylene-3:4-dicarboxylic anhydride, m.p. 296°, which with basic Cu carbonate in boiling quinoline or soda-lime at 180—300° gives 1:2-cyclopentenotriphenylene-3(or 4)-, m.p. 299—300° (Me ester, m.p. 197—198°), and -4(or 3)-carboxylic acid, m.p. 249° (Me ester, m.p. 117°), respectively. The former acid is converted by heating with Zn dust or as K salt alone at 320—350°, the latter by boiling with basic Cu carbonate in quinoline, into (III), b.p. 260—280°/2.5 mm. (picrate, m.p. 165—167°). The structure assigned to (II) is proved by its absorption spectrum and fluorescence. Dicyclohexenyl and indene at 180° give forms, b.p. 180—185°/0.3 mm. and 185—190°/0.3 mm., of dodecahydro-1:2:3:4-dibenzfluorene, dehydrogenated by Se at 300° to (II). 9-Chloromethylphenanthrene (prep. from the carbinol by



SOCl_2 and NPhMe_2 in C_6H_6 at 0°) and Et sodio-cyclohexanone-2-carboxylate in PhMe give Et 2-9'-phenanthrylmethylcyclohexanone-2-carboxylate, m.p. 118—119°, converted by 2:1 (vol.) $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ into the substance (IV), m.p. 250°. R. S. C.

Synthesis of 4:9- and 4:10-dimethyl-1:2-benzanthracene. L. F. FIESER and R. N. JONES (J. Amer. Chem. Soc., 1938, 60, 1940—1945).—Carcinogenic activity of 1:2-benzanthracene derivatives is connected with meso (9 or 10) and α (4, 5, or 8) substituents; 1:2:3:4- H_4 -derivatives may also be active. Two new such aromatic compounds and their H_4 -derivatives are prepared. 9:10-Dimethyl-1:2-benzanthracene and 1':2':3':4'-tetrahydro-4:10-ace-1:2-benzanthracene are highly carcinogenic. The structure of 6-methyl-1:2:3:4-tetrahydronaphthalene and 7-o-carboxybenzoyl-6-methyl-1:2:3:4-tetrahydronaphthalene (I) (modified prep.), m.p. 167.5—168° [Schroeter (A., 1921, i, 861), m.p. 160°], is proved by reactions detailed below and by oxidation of (I) by HNO_3 to 1:2:4:5- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$. With $\text{Zn}-2\text{N}-\text{NaOH}$ (I) gives 7-o-carboxybenzyl-6-methyl-1:2:3:4-tetrahydronaphthalene, m.p. 168.9—169.1°, converted by $\text{ZnCl}_2-\text{AcOH}-\text{Ac}_2\text{O}$ into 4-methyl-1':2':3':4'-tetrahydro-1:2-benz-9-anthranil acetate, m.p. 150.5—151°, which with MgBu^nBr gives 4-methyl-1':2':3':4'-tetrahydro-1:2-benz-9-anthrone (II), m.p. 151.5—151.7°. With MgMeCl (II) gives 4:9-dimethyl-1':2':3':4'-tetrahydro-1:2-benzanthracene, m.p. 62.4—62.8° (picrate, m.p. 135.8—136.2°), which with S at 180—210° in N_2 gives 4:9-dimethyl-1:2-benzanthracene, m.p. 75.1—75.5° (picrate, m.p. 116—116.4°), but Se at 300° causes loss of the meso-Me and leads to 4-methyl-1:2-benzanthracene (III). With $\text{Zn}-2\text{N}-\text{NaOH}$ (II) gives 4-methyl-1':2':3':4'-tetrahydro-1:2-benzanthracene, m.p. 82.3—82.9° (picrate, m.p. 158—158.2°), converted by Se at 290—300° into (III) [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ additive compound, m.p. 163.5—164°]. MgMeCl and (II) give the lactone, m.p. 115—115.5°, of 7- α -hydroxy- α -o-carboxyphenylethyl-6-methyl-1:2:3:4-

tetrahydronaphthalene, reduced by Zn-Hg-AcOH-HCl-PhMe to 7- α -*o*-carboxyphenylethyl-6-methyl-1:2:3:4-tetrahydronaphthalene, forms, m.p. 147–148° and 165.5–166°, respectively, cyclised by H₂SO₄ at room temp. to 4:10-dimethyl-1':2':3':4'-tetrahydro-1:2-benz-9-anthrone, m.p. 112.8–113.4°. Zn dust in NaOH-PhMe reduces this to 4:10-dimethyl-1':2':3':4'-tetrahydro-1:2-benzanthracene, m.p. 105–105.5° (picrate, m.p. 146–147°), dehydrogenated by S at 190–215° in N₂ to 4:10-dimethyl-1:2-benzanthracene, m.p. 114–114.4° (sinters at 113°) (picrate, m.p. 161.5–162°). M.p. are corr. R. S. C.

Mol. wt. of fichtelite.—See A., 1938, I, 502.

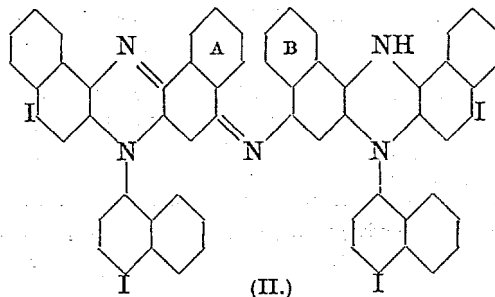
β -Phenylethylamine derivatives. Tertiary and quaternary salts. J. S. BUCK, R. BALTZLY, and W. S. IDE (J. Amer. Chem. Soc., 1938, 60, 1789–1792).—Directions are given for the prep. of OR·C₆H₄·[CH₂]₂·NMe₂ from OR·C₆H₄·CHO by way of the azlactones, pyruvic acids and oximes, and aryl-acetonitriles, the last step being Pd-hydrogenation in MeOH in presence of an excess of NHMe₂. The alkoxyamines are hydrolysed to the OH-amine by HCl at 160° in CO₂. The following are described: 4-*o*-, m.p. 186°, -*m*-, m.p. 123°, and *p*-ethoxy-, m.p. 168°, 4-3'-methoxy-2'-ethoxy-, m.p. 140°, and 4-3':4'-diethoxy-benzylidene-2-phenyloxazolone, m.p. 161°; *o*-methoxy-, m.p. 161°, *o*-, m.p. 164°, -*m*-, m.p. 132°, and *p*-ethoxy-, m.p. 182°, 3-methoxy-2-ethoxy-, an oil, and 3:4-diethoxy-phenylpyruvic acid, m.p. 164°; *m*-ethoxy-, b.p. 141°/8 mm., 3-methoxy-2-ethoxy-, b.p. 133°/2 mm., and 4-methoxy-3-ethoxy-phenylacetone, b.p. 151°/2.5 mm., m.p. 61.5°; dimethyl- β -phenylethylamine hydrochloride, m.p. 165° (corresponding methochloride, m.p. 192°); β -*o*-, m.p. 159.5° (221°), -*p*-, m.p. 176.5° (206°), and -*m*-methoxy-, m.p. 135° (158°), -3:4-, m.p. 197° (206°), and -2:3-dimethoxy-, m.p. 140° (180°), -*m*-, m.p. 137° (160°), -*p*-, m.p. 175° (193°), and -*o*-ethoxy-, m.p. 143° (211°), -3-methoxy-2-ethoxy-, m.p. 145° (182°), -3-methoxy-4-ethoxy-, m.p. 151° (173°), -4-methoxy-3-ethoxy-, m.p. 161.5° (162°), -3:4-diethoxy-, m.p. 138° (125°), -*o*-, m.p. 108° [254° (decomp.)], -*m*-, m.p. 164° (220°), and -*p*-hydroxy-, m.p. 181° [287° (decomp.)], -3:4-, m.p. 127° [263° (decomp.)], and -2:3-dihydroxy-phenyldimethylamine hydrochloride, m.p. 96° (225°), the m.p. in parentheses being those of the corresponding arylethyltrimethylammonium chlorides. Temp. are corr. R. S. C.

Thermal rearrangement of *N*-chloroacetanilide in aqueous solution. A. R. OLSON and J. C. HORNEL (J. Org. Chem., 1938, 3, 76–89; cf. A., 1937, II, 491).—In 20% aq. EtOH at 40° NPhClAc (I) reacts (A) with H⁺ and Cl⁻ to give a steady-state concn. of Cl₂ and NHPhAc, which subsequently react to give *o*- and *p*-C₆H₄Cl·NHAc and HCl (cf. Orton *et al.*, Proc. C.S., 1909, 25, 233), and (B) by condensation of 3 mols. of (I) to give an unknown compound (II) and two Cl⁻. With [Cl⁻] initially 0.04M and 0.005M about 70 and 25% respectively, of (I) disappears by reaction (A). (II) is an oxidising agent, and in acid solution oxidises I' instantaneously, Br' fairly rapidly, and Cl' very slowly. The initial rate of formation of (II) \propto initial (I) concn. and [H⁺], but independent of [Cl⁻], and is somewhat lowered by

increasing [EtOH]. (II) decomposes slowly into a non-oxidising compound and a Cl⁻. H. G. M.

Associating effect of the hydrogen atom. III. Further examples of steric interference between vicinal groups. H. O. CHAPLIN and L. HUNTER (J.C.S., 1938, 1034–1038).—Association factors are calc. cryoscopically in C₁₀H₆, or from wet m.p., as before (A., 1938, II, 179). Of 2:4:1- (I), 3:4:1- (II), and 2:3:1-(NO₂)₂C₆H₃·NHAc (III), (I) is unassociated, (II) associated, and (III) intermediate in properties. *Et* 4-nitro-3-acetamidobenzoate, m.p. 92° (from Ag salt), like *o*-NO₂·C₆H₄·NHAc (IV), is unassociated, but 2:3:5-NO₂·C₆H₃Br₂·NHAc and *Et* 2-nitro-3-acetamidobenzoate, m.p. 133°, are associated, as is 2:1:3-NO₂·C₆H₃Me·NHAc (from wet m.p. only). It thus appears that 3-substitution in (IV) hinders chelation (and favours association), owing to rotation of the NO₂-group into a position not coplanar with the C₆H₅ nucleus. Comparison between 1:8:2- and 1:6:2-(NO₂)₂C₁₀H₅·NHAc is difficult, owing to low solubility in C₁₀H₆, but the former is more associated (less chelated). In compounds of type 2:3:4-(NO₂)₂C₆H₃X·NHAc, it is suggested that X, if large, can orient the 3-NO₂ transversely to the nucleus, and favour chelation of the 2-NO₂; thus 2:3:4:1-(NO₂)₂C₆H₂Br·NHAc is much less, and 2:3:1:4-(NO₂)₂C₆H₂Me·NHAc rather less, associated than (III), although 2:3:4:1-(NO₂)₂(OEt)C₆H₂·NHAc is more associated. 2:5:4:1-(NO₂)₂C₆H₂Br·NHAc and 2:5:1:4-(NO₂)₂C₆H₂Me·NHAc are comparatively unassociated, and (from wet m.p. only) 2:3:4:1- and 3:5:4:1-(NO₂)₂(OMe)C₆H₂·NHAc are associated. Association-concn. curves and m.p. data are recorded. Attempted esterification (Fischer-Speier) of 2:3:1-(NO₂)(NHAc)C₆H₃·CO₂H gives *Et* 2-nitro-3-aminobenzoate, m.p. 48–49°, and the expected ester. E. W. W.

Catalytic phenylation of α -naphthylamine. H. H. HODGSON and E. MARSDEN (J.C.S., 1938, 1181–1182; cf. A., 1937, II, 408).—NH₂I, HI, and I catalyse the phenylation (*p*-tolyl- and α -naphthyl-ation) of α -C₁₀H₇NH₂ (I) with decreasing efficiency, the first giving the best yield (96%) of α -C₁₀H₇NHPh, almost free from aposafranine-like dyes. *p*-C₆H₄I·NH₂



and excess of (I) at 100° for 24 hr. yield two dyes, C₆₀H₃₃N₅I₄ (II), decomp. ~260°, and C₅₂H₂₅N₅I₄, i.e., (II) without rings A and B, decomp. ~280° (main product), the former being obtained also from I and (I) at 50–55°. NH₂Ph and NH₂Ph·HI at 198° give only a little NHPh₂. A. T. P.

Introduction of nitrogen into the sterol molecule. II. Partial synthesis of norcholanylamine.

M. VANGHELOVICI (Bul. Soc. Chim. România, 1937, 19, 35—42; cf. A., 1936, 982).—Et cholinate and $N_2H_4 \cdot H_2O$ in EtOH yield *cholanhydrazide* (+EtOH), m.p. 195° (Ac derivative, m.p. 235°), converted by AcOH-NaNO₂ into the *azide*, m.p. 96—98° (decomp.), and thence (EtOH) into the *urethane*, m.p. 135°, which when distilled with CaO at 9 mm. gives *norcholanylamine*, m.p. 95° (Ac derivative, m.p. 177°; *hydrochloride*, decomp. 285°). J. D. R.

Manufacture of carbimides.—See B., 1938, 1016.

Preparation of benzenesulphonylamides.—See B., 1938, 1100.

Conversion of *p*-substituted methylenebisarylamines and trimeric methylenearylamines into substituted 2-aminobenzylarylamines. T. R. MILLER and E. C. WAGNER (J. Amer. Chem. Soc., 1938, 60, 1738—1741).—Conditions are detailed for the prep. of 2 : 4-NH₂·C₆H₃X·CH₂·NH·C₆H₄Y·*p* (X = Y = Me, Cl, or Br) in good yield from *p*-C₆H₄Y·NH₂ (large excess) and *p*-C₆H₄Y·NH₂·HCl with (*p*-C₆H₄X·NH)₂CH₂ or (*p*-C₆H₄X·N·CH₂)₃. The prep. fails when X = Y = OMe or OEt, and gives tars when X ≠ Y. R. S. C.

Synthesis of naganine. O. J. MAGIDSON, O. S. MADAEVA, and M. V. RUBTZOVA (Chim. Farm. Prom., 1935, 2, 89—94).—1 : 4 : 6 : 8-NH₂·C₁₀H₄(SO₃H)₃ is condensed in H₂O with *m*-nitrotoluoyl chloride, the NO₂ reduced (Fe) to NH₂, and the amine condensed with *m*-NO₂·C₆H₄·COCl. The new NO₂ is reduced and the amine condensed with COCl₂ in NaOAc to the Na salt of *mm'*-bis-[5-(4 : 6 : 8-trisulpho-1-naphthyl-carbamyl)-*o*-tolylcarbamyl]carbanilide (naganine). CH. ABS. (c)

Azo-dyes derived from quinol. C. STAHLING and M. BADER (Bull. Soc. chim., 1938, [v], 5, 1171—1178).—Gradual addition of ClSO₃H to quinol in CHCl₃-C₅H₅N at 60° gives *dipyridinium phenylene-*p*-disulphate* (I), decomp. 170—180°, converted by NaOH into the salt C₆H₄(O·SO₃Na)₂·2H₂O, decomp. 110°; the mother-liquors from (I) with aq. Na₂CO₃ give *Na p-hydroxyphenyl sulphate* (+2H₂O) (II) which becomes partly liquid at 248—250°. *p*-OH·C₆H₄·OBz in CHCl₃-C₅H₅N and ClSO₃H afford *pyridinium p-benzoyloxyphenyl sulphate*, decomp. 124—134° [corresponding Na salt, melting partly at 256° (decomp.)]. Debenzoylation is readily effected by hot aq. Na₂CO₃. When coupled with the requisite ArN₂X, (II) affords Na 3-benzeneazo-, 3-*p*-tolueneazo-, and 3-*p*-nitrobenzeneazo-4-hydroxyphenyl sulphate. Na 3-2' : 5'-dichlorobenzeneazo-4-hydroxyphenyl sulphate, sublimes at 190°, decomposes ~250°, is readily converted by HCl into 2 : 5-dichloro-2' : 5'-dihydroxyazobenzene, which changes in cryst. form at ~224° and melts ~246°. The following compounds are obtained similarly: Na 3-4'-nitro-2'-methylbenzeneazo-4-hydroxyphenyl sulphate, m.p. 190° (decomp.), and 4-nitro-2' : 5'-dihydroxy-2-methylazobenzene, m.p. 206—208°; Na 3-4'-anilino-2' : 5'-diethoxybenzeneazo-4-hydroxyphenyl sulphate, m.p. 248°, converted by HCl into a substance, m.p. 88—90°; Na 3-5'-chloro-2'-phenoxybenzeneazo-4-hydroxyphenyl sulphate, m.p. 170—172°, and 5-chloro-2' : 5'-dihydroxy-2-phenoxyazobenzene, m.p. 204—206°.

These dyes and those obtained correspondingly from 1 : 4-C₁₀H₈(OH)₂ are without tinctorial val.

H. W.

Action of weak reducing agents on diazo-compounds. O. M. GOLOSENKO (Prom. Org. Chim., 1938, 5, 479—484).—The author's method of determination of diazo-compounds (A., 1937, II, 188) is of general application. R. T.

[Reaction of nitrosyl fluoborate with aniline.]—See A., 1938, I, 532.

Decomposition reactions of aromatic diazo-compounds. V. Reactions of benzenediazonium chloride with sulphur, selenium, and tellurium. W. A. WATERS (J.C.S., 1938, 1077—1078; cf. A., 1938, II, 342).—Solid PhN₂Cl with Te and CaCO₃ in cold COMe₃ gives TePh₂Cl₂; S at > 50° affords COMe·CH₂Cl, Ph₂S, and (probably) Ph₂S₂, and Se on heating yields Ph₂Se. This supports the view (A., 1938, II, 52) that free Ph is present. PhN₂Cl does not appear to react with red P, B, or Si.

E. W. W.

Depression of m.p.—See A., 1938, I, 507.

Cineole method for determination of *o*-cresol.—See B., 1938, 1013.

Mechanism of halogenation of phenols. E. A. SCHILOV (J. Gen. Chem. Russ., 1938, 8, 519—523).—Polemical against Lichoscherstov *et al.* (A., 1938, II, 37). R. T.

Halogen derivatives of α -ethylpropylcresols.—See B., 1938, 1101.

Syntheses with *o*- and *p*-hydroxydiphenyls. II. Nitro- and amino-hydroxydiphenyls, their derivatives, and azo-dyes from hydroxydiphenyls. N. N. VOROSHOV, jun., and A. T. TROSCHTSCHENKO (J. Gen. Chem. Russ., 1938, 8, 431—437).—*o*-C₆H₄Ph·OH and HNO₃ in AcOH at 0° give a mixture of 3-nitro- (I), m.p. 62° (*Me ether*, m.p. 72—73°), and 5-nitro-2-hydroxydiphenyl. Further nitration of (I) yields successively 3 : 5-dinitro- and tetranitro-2-hydroxydiphenyl, m.p. 182—183°. (I) is reduced (SnCl₂ in EtOH) to 3-amino-2-hydroxydiphenyl (II), m.p. 121—122.5°, which with AcCl in C₆H₆ (3 hr. at the b.p.) yields 6-phenyl-1-methylbenzoxazole, m.p. 69—70°; with BzCl the product is 1 : 6-diphenylbenzoxazole, m.p. 114—116°. (II), (I), and glycerol heated with H₂SO₄ yield 8-hydroxy-7-phenylquinoline, m.p. 142—144° (*hydrochloride*, m.p. 208—209°; Cu salt). 3-Amino- and 3-nitro-4-hydroxydiphenyl give similarly 8-hydroxy-5-phenylquinoline, m.p. 91—92° (*hydrochloride*, m.p. 212—226°; Cu salt). Diazotised (II) and β -C₁₀H₇·OH yield 2-hydroxy-3- β -hydroxynaphthaleneazodiphenyl, m.p. 211—211.5°; an analogous compound with *m*-C₆H₄(OH)₂ is described. 4-Hydroxydiphenyl gives azo-dyes with diazotised *p*-NH₂·C₆H₄·NO₂, m.p. 174—175°, α -C₁₀H₇·NH₂, m.p. 121—123°, and with tetrazotised benzidine, 3 : 3'-dimethyl- and 3 : 3'-dimethoxy-benzidine.

R. T.

Relations between the chemical constitution of substituted phenols and of ascorbic acid and the size of their solubility products with anti-pyrine and pyridine.—See A., 1938, I, 518.

Arylphosphoric acid halides.—See B., 1938, 1018.

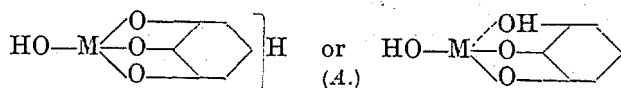
Manufacture of triaryl phosphates.—See B., 1938, 1015.

Substitution reactions and meso-derivatives of 1:2-benzanthracene. L. F. FIESER and E. B. HERSHBURG (J. Amer. Chem. Soc., 1938, 60, 1893—1896).—The 9-position of 1:2-benzanthracene (I) is shown to be remarkably inert. With $\text{Pb}(\text{OAc})_4$ in AcOH at 100° (I) gives 52% of pure 1:2-benz-10-anthranyl acetate, but 10-methyl-1:2-benzanthracene gives only 10-acetoxymethyl-1:2-benzanthracene, m.p. $150.5\text{--}151.5^\circ$ (17%), the 9-position being unattacked. Prep. by cyclisation methods of 10-anthranyl acetate, 3-methoxy-1:2-benz-10-anthranyl acetate, m.p. $194\text{--}194.5^\circ$, and 1-keto-1':2':3':4'-tetrahydro-8:9-acephenanthrene, m.p. $143\text{--}145^\circ$, is improved. 10-Methyl-1:2-benz-9-anthranyl (II), m.p. $153.5\text{--}154^\circ$, and -3-anthranyl acetates (III), m.p. $214\text{--}215^\circ$, are prepared. When MgBu^aBr and (III) are heated in Et_2O and then treated with $\text{Me}_2\text{SO}_4\text{--C}_6\text{H}_6$, 53% of 3:10-dimethoxy-1:2-benzanthracene (?), stable, m.p. $146\text{--}146.5^\circ$, and unstable forms, m.p. $84\text{--}87^\circ$, is obtained; by a similar reaction (II) gives 9-methoxy-10-methyl-1:2-benzanthracene, m.p. $143\text{--}144^\circ$. 1:2:5:6-Dibenzanthracene is best purified (to m.p. $266\text{--}266.5^\circ$) by treatment with $\text{Pb}(\text{OAc})_4$, which by oxidation removes any 1:2:6:7-dibenzanthracene present. The structure of 10-nitro-1:2-benzanthracene, m.p. $164\text{--}165^\circ$ (Barnett *et al.*, A., 1925, i, 821), is proved by PtO_2 -hydrogenation to the 10- NH_2 -derivative, m.p. $174.5\text{--}175.5^\circ$, which is also obtained from the 10-OH-compound (IV), NH_3 , and NaHSO_3 in aq. dioxan at 150° . 10-Allyl-1:2-benzanthracene, I, and AgOBz in hot C_6H_6 give γ -1:2-benz-10-anthranyl-propane- α -diol dibenzoate, m.p. $152.5\text{--}153.5^\circ$. With Bu^aOCl in Et_2O (IV) gives a Cl-compound, $\text{C}_{18}\text{H}_{18}\text{OCl}$, m.p. $197\text{--}198^\circ$ (decomp.), converted by hot MeOH into a bimol. product, $\text{C}_{36}\text{H}_{22-24}\text{O}_2$, m.p. $261\text{--}263^\circ$, previously (A., 1937, II, 333) obtained directly from (IV). 3:4-Benzpyrene and methylcholanthrene with $\text{Pb}(\text{OAc})_4$ give OAc-derivatives, m.p. $208.5\text{--}209^\circ$ and $179.5\text{--}180.5^\circ$, respectively. M.p. are corr.

R. S. C.

Constitution of (A) bismuth pyrogallate, (B) antimony pyrogallate, (C) antimony subgallate. S. TAKAGI and Y. NAGASE (J. Pharm. Soc. Japan, 1936, 56, 161—169, 170—174, 175—179).—(A) Pyrogallol (I) and $\text{Bi}(\text{NO}_3)_3$ in aq. AcOH give pyrogallomonobismuthic acid ($+\text{H}_2\text{O}$) (A; $\text{M} = \text{Bi}$) which forms a Ba salt but does not ppt. $\text{Bi}(\text{OH})_3$ in alkaline solution and gives no colour with FeCl_3 . Bi salts of the Me ether, amide, and anilide of (I) are described.

(B) (I) and $\text{C}_4\text{H}_4\text{O}_6\text{K}(\text{SbO})$ in H_2O at $40\text{--}50^\circ$ give Sb pyrogallate ($+0.5\text{H}_2\text{O}$) (A; $\text{M} = \text{Sb}$), which gives



colours with FeCl_3 and reduces AgNO_3 and KMnO_4 . Methylation (Me_2SO_4) gave (?) $\text{C}_6\text{H}_3\text{Me}_3$.

(c) Gallic acid and $\text{C}_4\text{H}_4\text{O}_6\text{K}(\text{SbO})$ in boiling H_2O give Sb subgallate, $[\text{OHSbO}_3\text{C}_6\text{H}_2\text{COO}]_2\text{H}_2 + 2\text{H}_2\text{O}$,

similar in properties to Sb pyrogallate. Methylation (Me_2SO_4) gave trimethylgallic acid. CH. ABS. (c)

Modes of reaction of organo-metallic compounds. II. Action of Grignard's compounds on phenyl allyl ether. A. LÜTTRINGHAUS, G. VON SÄÄF, and K. HAUSCHILD (Ber., 1938, 71, [B], 1673—1681).— $\alpha\delta$ -Dibromo- Δ^8 -butene (I) [from butadiene (II) and B in CHCl_3 at -15° to -18°] with NaI in COMe_2 yields I and (II), whilst with Zn or Mg in a suitable solvent it affords (II) in good yield. (I) and KOPh in MeOH afford α -bromo- δ -phenoxy- Δ^8 -butene (III), b.p. $104\text{--}105^\circ/0.07\text{ mm.}$, transformed by KOPh into $\alpha\delta$ -diphenoxy- Δ^8 -butene, m.p. 90° . (III) and KMnO_4 in COMe_2 containing MgSO_4 at -5° give α -bromo- $\beta\gamma$ -dihydroxy- δ -phenoxybutane, m.p. 111.5° , further oxidised to $\text{CH}_2\text{Br}\text{--CO}_2\text{H}$ and $\text{OPh}\text{--CH}_2\text{--CO}_2\text{H}$. (III) is transformed by Mg or MgBuBr into (II) and PhOH . Ph allyl ether (IV) and MgBuBr afford PhOH and Δ^a -*n*-heptene (dibromide, b.p. $98\text{--}100^\circ/11\text{ mm.}$; oxidised to hexoic acid). MgPhBr and (IV) give PhOH and allylbenzene. PhOH , pentadecene, and tetracosane are derived from Mg dodecyl bromide and (IV). Guaiacol allyl ether and MgBuBr afford guaiacol and heptene but no $o\text{-C}_6\text{H}_4(\text{OH})_2$. Ph cinnamyl ether and MgPhBr give PhOH in 51% yield. $\text{CH}_2\text{Ph}\text{--OPh}$ is little changed by MgBuBr at 80° . H. W.

Preparation of diphenyl ether. M. A. ELENEVSKI and Z. G. ARTAMONOVA (J. Gen. Chem. Russ., 1938, 8, 507—509).—A mixture of PhOH 23.5, PhCl 22.5, KOH 11.2, and CuCO_3 0.5 g. is heated at the b.p. for 9 hr., so that PhCl distils, is separated from H_2O , and returned. The yield of Ph_2O is 59—64%.

R. T.

Action of gaseous hydrogen chloride on 5-nitroso-*o*-cresol and 6-nitrosothymol. A. ANGELLETI and A. OLIVERIO (Gazzetta, 1938, 68, 359—363).—2:1:5-OH: $\text{C}_6\text{H}_4\text{Me}$:NO with HCl in dry Et_2O gives the hydrochloride of 3:4-dichloro-5-aminocresol, m.p. $158\text{--}159^\circ$ (Ac derivative, m.p. 160°), which by diazotisation yields 1:3:4:2:5- $\text{C}_6\text{HMeCl}_2(\text{OH})_2$ (Me_2 ether, m.p. 65°). 6-Nitrosothymol similarly gives the hydrochloride, m.p. $190\text{--}195^\circ$ (decomp.), of 5-chloro-6-aminothymol, m.p. 115° (decomp.). E. W. W.

Anomalous reaction of the sodium salt of 4-nitro-1-thiolnaphthalene with 2-chloro-1-nitronaphthalene and with *o*-chloronitrobenzene. H. H. HODGSON and E. LEIGH (J.C.S., 1938, 1031—1034).— $\text{NO}_2\text{--C}_{10}\text{H}_6\text{--SNa}$ (obtained by treating $\text{C}_{10}\text{H}_6\text{Cl}\text{--NO}_2$ with $\text{EtOH}\text{--Na}_2\text{S}_2$, boiling the product with aq. $\text{EtOH}\text{--Na}_2\text{S}\text{--NaOH}$, and filtering off the insol. monosulphide) with $\text{C}_{10}\text{H}_6\text{Cl}\text{--NO}_2$ gives in most cases the expected dinitrodinaphthyl sulphides. Thus 1:2- (I) and 1:4- $\text{C}_{10}\text{H}_6\text{Cl}\text{--NO}_2$ (II) (using either compound and the SNa compound derived from the other) give 2:4'-dinitro-1:1'-dinaphthyl sulphide, m.p. $162\text{--}163^\circ$. Similarly (I) and 2:1- $\text{C}_{10}\text{H}_6\text{Cl}\text{--NO}_2$ (III) give, by either route, 1:2'-dinitro-2:1'-dinaphthyl sulphide, m.p. $172\text{--}173^\circ$. 1:2- $\text{NO}_2\text{--C}_{10}\text{H}_6\text{--SNa}$ and (II) give 1:4'-dinitro-2:1'-dinaphthyl sulphide (IV), m.p. $125\text{--}126^\circ$, but (III) and 4:1- $\text{NO}_2\text{--C}_{10}\text{H}_6\text{--SNa}$ afford not (IV) but 4:4'-dinitro-1:1'-dinaphthyl

sulphide (A., 1937, II, 414). It is suggested that after separation of Cl⁻, the 4-H in 1-NO₂-C₁₀H₆⁺ is very rapidly ionised (owing to the effects of NO₂ and of the positive 2-C pole), and that S (rendered less reactive by the 4-NO₂) then reacts at the new ionic centre. Similarly, o-C₆H₄Cl·NO₂ and 4:1-NO₂-C₁₀H₆·SNa give the anomalous product, *p*-nitrophenyl 4-nitro-1-naphthyl sulphide, m.p. 236—238°, also obtained from (II) and *p*-NO₂-C₆H₄·SNa, which with (I) and (III) gives *p*-nitrophenyl 2-nitro-1-, m.p. 121—122°, and 1-nitro-2-naphthyl sulphide, m.p. 122—123°, respectively. o-NO₂-C₆H₄·SNa with (I), (III), and (II) gives o-nitrophenyl 2-nitro-1-, m.p. 196—197°, 1-nitro-2-, m.p. 162—163°, and 4-nitro-1-naphthyl sulphide, m.p. 157—158°, respectively. Colour reactions of the sulphides with conc. H₂SO₄, ClSO₃H, and 26% oleum are given. E. W. W.

Purification of β-phenylethyl alcohol.—See B., 1938, 1018.

Active cyclohexane compounds. M. MOUSERON and R. GRANGER (Compt. rend., 1938, 207, 366—368).—Interaction of MgAlkX with active 3-methylcyclohexanone affords *cis*- and *trans*-3-methyl-1-alkylcyclohexanols, the less volatile of which are obtained pure. The following are described: 3-methyl-, 1:3-dimethyl- (phenylcarbamate, m.p. 84°), 3-methyl-1-ethyl- (phenylcarbamate, m.p. 94°), 3-methyl-1-*n*-propyl- (phenylcarbamate, m.p. 111°), and 3-methyl-1-*n*-butyl-cyclohexanol. The ratio between the optical rotation of the alcohols in EtOH or C₆H₆ and that without a solvent increases slightly in the order given above. The alcohols are dehydrated to the active isomeric cyclohexenes, viz., methyl-, b.p. 102.5° and 104°/760 mm., 1:3-dimethyl-, b.p. 127°/760 mm., 1:3-dimethyl-Δ³- (I), b.p. 129°/760 mm., 1-methyl-3-ethyl-, b.p. 148° and 150°/760 mm., 1-methyl-3-*n*-propyl-, b.p. 170° and 171°/760 mm., and 1-methyl-3-*n*-butyl-cyclohexene, b.p. 180°/760 mm. These with H₂-Pt afford *cis*- and *trans*-cyclohexanes; the following are described: 1:3-dimethyl-, b.p. 119.5° (optically inactive) and 123.5°/760 mm., 1-methyl-3-ethyl-, b.p. 147.5° and 148.5°/760 mm., and 1-methyl-3-*n*-propyl-cyclohexane, b.p. 168.7° and 169.2°/760 mm. The less volatile isomeride has the *trans*-configuration (cf. A., 1936, 61). 1-Methyl-3:4-, b.p. 146.5°/760 mm., 1:3-dimethyl-2:3-, b.p. 152.5°/760 mm., and -3:4-, b.p. 152°/760 mm., 1-methyl-3-ethyl-3:4-, b.p. 174°/760 mm., and 1-methyl-3-*n*-propyl-3:4-epoxycyclohexane, b.p. 190°/760 mm., are prepared from the appropriate cyclohexene and BzO₂H. 2-Amino-2:4-dimethyl-, b.p. 111°/20 mm., and -4-methyl-2-ethyl-cyclohexanol, b.p. 120°/20 mm., are purified through the H tartrates. (I) is oxidised (KMnO₄) to active β-methyladipic acid. Vals. of [α] and other physical data are given.

J. L. D.

Dipole moments and molecular structure.
XIX. Dipole moments of anthracene derivatives and the stereochemical mechanism of addition and splitting reactions in the anthracene series. E. BERGMANN and (MISS) A. WEIZMANN (J. Amer. Chem. Soc., 1938, 60, 1801—1804; cf. A., 1936, 1183).—Dipole moments show that 9:10-addition of Cl₂ to 1:5-dichloroanthracene (I) and

9:10-diphenylanthracene is a reaction of the Cl₂ mol., since the product is the *cis*-derivative, but that 1:8-dichloroanthracene gives the *trans*-compound. 1:5-Dichloro-9:10-dihydroxy-9:10-dihydroanthracene, m.p. 210°, is the *cis*-diol, the isomeride, m.p. 244°, the *trans*-diol. The α- and β-forms of Me₂ 9:10-dihydroanthracene-9:10-dicarboxylate (A., 1928, 1036) are *trans* and *cis*, respectively. 1-Chloroanthraquinone has a high dipole moment (1.9) due, probably, to induction or resonance. Prep. of the most of the compounds named is modified. 1:5:9:10-Tetrachloro-, m.p. 214—215°, and 1:5-dichloro-9:10-dibromo-9:10-dihydroanthracene, m.p. 220° (decomp.), are obtained from (I), which is prepared with 1:5-dichloro-9-hydroxy-9:10-dihydroanthracene, m.p. 102—103°, from 1:5-dichloroanthraquinone, Zn dust, and hot 20% aq. NH₃. The fission of 9:10-Cl₂-compounds does not appear to follow definite rules. R. S. C.

Structure of cholesteryl chloride. E. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 1997—1998).—The absence of Walden inversion when cholesteryl chloride reacts with NaOAc and chloroandrosterone with NaOBz indicates that these chlorides can react in the allylic (Δ⁴) form. R. S. C.

Bombicestrol. I. K. KAWASAKI (J. Pharm. Soc. Japan, 1935, 55, 758—774).—*Bombicestrol* (I), C₂₇H₄₆O, had m.p. 139—140°, [α]_D²⁵ -31.5° (all rotations are in CHCl₃) and gave colour reactions of cholesterol. The *acetate* (I), m.p. 130.5°, [α]_D²⁷ -44.2°, *benzoate*, m.p. 147°, [α]_D¹⁶ -14.1°, and *dibromide*, m.p. 114—115°, were prepared. *Bombicesteryl chloride*, m.p. 84—86°, with Na + C₅H₁₁·OH gave *bombicestene*, m.p. 91—92°, [α]_D²⁶ -58.2° (*dibromide*, m.p. 91—93°), which was reduced catalytically to *bombicestane*, m.p. 79° (no depression with cholestane). *Bombicestanol*, m.p. 134—135°, [α]_D²³ -10.6° (*acetate*, m.p. 130—131°, [α]_D¹⁷ +9.88°), *bombicestanone*, m.p. 152°, [α]_D²³ +37.9°, and *allobombicestrol*, m.p. 97°, were prepared by standard reactions. Oxidation of (I) gave a ketone probably identical with the methylheptanone obtained from cholesteryl acetate. CH. ABS. (c)

Satisterol, C₂₇H₄₆O, m.p. 156°, and its Ac, m.p. 111°, EtCO, m.p. 106°, and Bz, m.p. 129°, derivatives.—See A., 1938, III, 772.

Sterols. XLII. Isolation of œstranediols from human non-pregnancy urine. R. E. MARKER, E. ROHRMANN, E. J. LAWSON, and E. L. WITTLE. **XLIII. 3(β)-Hydroxysteroids in human pregnancy urine.** R. E. MARKER, S. B. BINKLEY, E. L. WITTLE, and E. J. LAWSON (J. Amer. Chem. Soc., 1938, 60, 1901—1903, 1904—1905; cf. A., 1938, II, 408).—**XLII.** The carbinol fraction of the sterols of human non-pregnancy urine contains as 3(β)-OH-compounds mainly cholesterol and, amongst the compounds not pptd. by digitonin, *œstranediol-A*, m.p. 242° (*diacetate*, m.p. 160°), and -B, m.p. 204° (*diacetate*, m.p. 160°; also obtained by PtO₂-hydrogenation of *œstrone* in HCl-EtOH), oxidised by CrO₃ to *œstranediolone-A*, m.p. 124°, and -B, m.p. 170°, and both converted by Pt-black in N₂ at 215—220° into *equilenin* and thus stereoisomeric at least at C₆₅ or C₁₀₀. *œstrone* is unaffected by enzyme extracts from hog ovaries, ox

adrenal glands, and bull testes. In the pregnant woman oestrone is not utilised and is thus excreted in large amount, the reduction products being absent, whereas progesterone is utilised and is thus excreted solely as its reduction products. In the non-pregnant woman these relations are reversed: oestrone is absent from the urine, but its reduction products (at any rate the two diols) are present. Neosterol and epineosterol are not pptd. by digitonin.

XLII. In confirmation of theory, saturated compounds of the coprostanol series with a 3(β)-OH are absent from human pregnancy urine (1000 gallons examined). The only 3(β)-OH-compounds present are cholesterol (4 mg. per gal.) and *allopregnane-3(β):20(α)-diol* (1—1.5 mg. per gal.). R. S. C.

Preparation of oestradiol from urine of mares.—See B., 1938, 1101.

Sterols. XLI. Reduction of naphtholic steroids to phenolic steroids. Equilenin. R. E. MARKER (J. Amer. Chem. Soc., 1938, 60, 1897—1900; cf. A., 1938, II, 415).—The reduction of β -naphtholic sterols by Na-C₅H₁₁-OH to H₄-derivatives, in which ring A is benzenoid, is a general reaction (cf. Marker *et al.*, A., 1936, 1256; Windaus *et al.*, A., 1937, II, 99); larger amounts of neutral products are also formed. Correlation of configurations of sterols by the behaviour with digitonin and the m.p. is unreliable; the only valid correlation is obtained by chemical reactions. Equilenin (I) (modified purification), m.p. 257—258°, $[\alpha]_D^{25} +89^\circ$, and Na-C₅H₁₁-OH give a phenolic product which when benzoylated, oxidised (CrO₃), and then hydrolysed affords oestrone. Al(OPrⁱ)₃ and (I) give α -(II), m.p. 248° (*Ac*₂, m.p. 124°, and *Bz* derivative, m.p. 215°), and β -dihydroequilenin (III), m.p. 215° (*Bz* derivative, m.p. 204° (cf. Marker *et al.*, A., 1937, II, 250). Wintersteiner's (II) (cf. A., 1937, II, 100) contained an active impurity (? α -oestradiol), since pure (II) and (III) have oestrogenic potencies of only 250 and 75—100 rat units per mg. Neither (II) nor (III) is pptd. by digitonin. With Na-C₅H₁₁-OH (II) gives a little α -oestradiol (IV), another phenol, m.p. 151—154°, and a neutral substance, m.p. 172°. (III) gives similarly β -oestradiol and other phenolic and neutral products; the benzoylated phenolic product with CrO₃ followed by hydrolysis gives oestrone and a substance, C₁₈H₂₀O₂, m.p. 222—225° [also obtained by oxidation of the mother-liquors from (IV)]. Oestrone benzoate and Al(OPrⁱ)₃ give after hydrolysis α - and β -oestradiol. R. S. C.

Steric hindrance. III. Index of unsaturation in the *cyclopentene* series. P. DUQUÉNOIS (Bull. Soc. chim., 1938, [v], 5, 1207—1208).—Hydnocarpic and chaulmoogric acid and their esters give theoretical Br vals. The *cyclopentene* nucleus is therefore readily accessible to Br under the conditions of Volmar and Samdahl (B., 1928, 236). H. W.

cycloHexane series. I. Synthesis of nitriles. G. VASILU (Bul. Soc. Chim. România, 1937, 19, 75—83; cf. A., 1938, II, 190).—*cycloHexyl* bromide (I) and CH₂Ph-CN in Et₂O with NaNH₂ yield *cyclohexylphenylacetonitrile* (II), m.p. 60°, converted by further treatment with (I) and NaNH₂ in Et₂O into

dicyclohexylphenylacetonitrile, m.p. 133°, also formed with (II) from CH₂Ph-CN, (I) (2 mols.), and NaNH₂. Similarly from the appropriate CN-CHPhAlk are obtained α -*cyclohexyl- α -phenyl-butylonitrile*, b.p. 179—180°/15 mm., and *valeronitrile*, b.p. 190—191°/18 mm. Hydrolysis of (II) with H₂SO₄ yields *cyclohexylphenylacetamide*, m.p. 174°, and with KOH-EtOH, *cyclohexylphenylacetic acid*. J. D. R.

Benzilic acid rearrangement. J. J. BLANKSMA and W. H. ZAAIJER (Rec. trav. chim., 1938, 57, 883—885).—The velocity of the rearrangement (*k*) and the amount of BzOH formed (side reaction) in the action of NaOH or KOH on benzil in EtOH or MeOH at 100° have been measured by titrating with HCl and also determining the unchanged benzil. Rearrangement occurs slightly faster with NaOH than with KOH in 100% MeOH; 90% MeOH leads to increase in *k*. For NaOH, *k*_{MeOH} is > *k*_{EtOH}. MeOH is the better solvent since EtOH gives some MeCHO and thence resin. Anisil under similar conditions gives anisic but practically no anisilic acid. A. LI.

Common basis of intramolecular rearrangements. IV. Correction: the benzilic acid rearrangement. F. C. WHITMORE (J. Amer. Chem. Soc., 1938, 60, 2002—2003).—The application of the author's theory (A., 1932, 1016) to the benzilic acid rearrangement is rendered invalid by later work of others. R. S. C.

Steric hindrance. II. Index of unsaturation in the *cinnamic* series. P. DUQUÉNOIS (Bull. Soc. chim., 1938, [v], 5, 1200—1207).—CHPh:CH₂ and CHPh:CH-CH₂-OH absorb Br quantitatively in 2 hr. in the dark. With CHPh:CH-CHO, CHPh:CH-CO₂H and its esters bromination is incomplete in the dark but complete after 2 hr. in sunlight. In the dark the Br vals. of these latter compounds are not const.; the rate of fixation of Br is a function of the halogen concn. and is inversely \propto the content of dissolved O₂. Steric hindrance appears to have a distinct relationship to the addition of Br. Inactivity is general among compounds with heterogenic conjugated double linkings. Addition takes place more readily with CHPh:CH-CO₂H than with its esters and is most difficult with CH₂Ph cinnamate. With cinnamyl cinnamate a supplementary passivity is observed, since after fixation of the first mol. of Br at the double linking of the alcoholic radical a relatively small space is left around the other ethylenic linking, thus greatly hindering the access of a new mol. of Br. Coumarin is always very incompletely brominated in spite of various photochemical stimuli. Cyclisation appears to increase the condition of saturation and the conjugated double linkings of this heterocyclic substance confer on it the properties of a nucleus. CH₂Ph α -*di*bromo- β -phenylpropionate has m.p. 95°. H. W.

Stereoisomeric enolic ethers, acetals, and the Claisen condensation. F. ARNDT and L. LOEWE [with E. ÖZSÖY, M. ÖGÜT, A. ARSLAN, and L. BAGEVI] (Ber., 1938, 71, [B], 1631—1640).—CH₂Bz-CN is transformed by CH₂N₂ in Et₂O into *trans- β -methoxycinnamonitrile* (I), b.p. 111.5°/1 mm., m.p. 31°, con-

verted by boiling MeOH-NaOMe (2—4 mols.) in 1—5 hr. into a mixture, b.p. 116—126°/1 mm., of *cyanacetophenone Me₂ acetal* (II), b.p. 111°/1 mm., m.p. 65.5°, and *cis-β-methoxycinnamionitrile* (III), b.p. 126°/1 mm. Neither (I) nor (III) is isomerised by heat. Transformation takes place through (II), since the same equilibrium is attained whether the starting point is (I), (II), or (III). NaOMe is pronouncedly catalytic. The enol ether (IV) of 2-hydroxythionaphthensulphone is quantitatively converted by warm NaOMe-MeOH into the corresponding acetal. Similarly the Meenoether of *p*-C₆H₄Me·SO₂·CH₂·COMe quantitatively affords the acetal (V), *p*-C₆H₄Me·SO₂·CH₂·CMe(OMe)₂, which does not undergo thermal re-conversion. In alkaline solution the equilibrium is completely on the acetal side. CH₂Bz·CN enolises spontaneously to a conjugated enol. (IV) and (V) on the contrary can be obtained only by indirect methylation with CH₂N₂ since the corresponding enols do not exist as they lack a conjugated system. The same constitutional factors are operative for the equilibria acetal-enol ether and keto-enol. As a further example of a conjugated enol ether CH₂Bz·CO₂Me is converted by CH₂N₂ into *Me cis-β-methoxycinnamate*, b.p. 124°/2 mm. The position of the equilibrium attained in boiling MeOH containing NaOMe is less readily ascertained owing to partial ester hydrolysis. If only 1 mol. of NaOMe is used the secondary change is not marked and the recovered ester is constitutionally pure enol ether. A transitory addition of OMe ion to at least a portion of the mols. is certain since the product has a lower and less const. b.p. and partly solidifies at -15°; obviously the pure *trans*-enol ether is solid and has a lower b.p. than the liquid *cis*-ether. With 4 mols. of NaOMe partial hydrolysis occurs with production of a solid Na salt and of a mixture of equimol. amounts of enol ether and acetal; repeated treatment and fractionation gives a product which is richer in acetal but not homogeneous. The chemistry of alkoxide catalysis and of the Claisen condensation is discussed in detail.

H. W.

Derivatives of oleic acid. G. ROBERTI, P. PIUTTI, and D. DINELLI (Ric. sci. Progr. tecn., 1936, [ii], 7, II, 10—12; Chem. Zentr., 1936, ii, 3536).—Phenylstearic acid (cf. A., 1927, 560) and glyceryl tri(phenylstearate) (I) have been prepared. A 1:1 mixture of (I) with olive oil remains liquid at a low temp. and is recommended as a lubricant for combustion engines.

A. H. C.

Racemisation of amino-acids.—See B., 1938, 1016.

***p*-cyclohexylphenoxyacetic acid and its derivatives.** D. BODROUX and A. CHATENET (Compt. rend., 1938, 207, 364—366; cf. A., 1929, 1050).—Na *p*-cyclohexylphenoxy with CH₂Cl·CO₂Na in boiling EtOH affords *p*-cyclohexylphenoxyacetic acid (I), m.p. 151—152° [Na (+3H₂O), Ba (+3H₂O), Ag, and NH₄ (+H₂O) salt; the last with aq. NH₃-CuSO₄ at 80° affords the Cu₄NH₃ (+H₂O) derivative which at 100° gives the Cu salt; Me (II), m.p. 39°, and Et, m.p. 32°, esters, obtained only by the Ag salt method]. (II) with NH₃ in aq. EtOH at 75° affords *p*-cyclohexylphenoxyacetamide, m.p. 169—170°. J. L. D.

Action of benzoic acid on vanadium pentoxide. J. F. LEVY (Bol. Soc. Quím. Peru, 1938, 4, 108—115).—An extension of earlier work (A., 1938, II, 189). A small excess of BzOH with V₂O₅ at 249° gives *hypovanadous benzoate*, V(OBz)₂, also prepared from V and PhCHO at room temp.; with C₅H₅N and quinoline it gives the corresponding vanadates (cf. Katzoff and Roseman, A., 1936, 1350). F. R. G.

Fixation of active nitrogen by organic compounds. L. B. HOWARD and G. E. HILBERT (J. Amer. Chem. Soc., 1938, 60, 1918—1924).—At N, produced by a condensed or uncondensed discharge, and C₂Ph₂ give HCN, a brown, amorphous solid (I) of high m.p., (?) PhCN, and (?) a carbimide. (I) contains 16—18% of N, is stable to acid, generates NH₃ with alkali, with HNO₃ gives BzOH and an acid, (C₁₀H₇O₅N)_x, m.p. 215—220°, and probably contains N·C·N. Tetrahydronaphthalene and PhCN give similar products.

R. S. C.

Industrial preparation of benzoyl chloride.—See B., 1938, 1013.

Estimation of isomeric nitrobenzoic acids. B. FLÜRSCHHEIM and E. L. HOLMES (J.C.S., 1938, 1242).—A correction of a statement of Ingold and Smith (A., 1938, II, 324).

A. T. P.

Titration of esters of *p*-hydroxybenzoic acid. F. REIMERS (Dansk Tidsskr. Farm., 1938, 12, 203—210).—Titration of *p*-OH·C₆H₄·CO₂H (I) as a dibasic (to *p*_H ~11) or monobasic (to *p*_H 6.8) acid, and direct titration of esters of (I), are unreliable. (I), from hydrolysis (aq. NaOH) of its esters, is determined accurately by the reaction: (I) + 3Br₂ → 2:4:6-C₆H₂Br₃·OH + 3HBr + CO₂, by addition of KBr-KBrO₃ in acid solution and determination of the excess of Br iodometrically.

M. H. M. A.

Syntheses with *o*- and *p*-hydroxydiphenyls. I. 4- and 2-Hydroxydiphenyl-3-carboxylic acids and their derivatives. N. N. VOROSHOV, jun., and A. T. TROSCHTSCHENKO (J. Gen. Chem. Russ., 1938, 8, 424—430).—*p*-C₆H₄Ph·OH, KOH, and CO₂ (5 hr. at 200—250°/30 atm.) yield 4-hydroxydiphenyl-3-carboxylic acid, m.p. 215—216° (Ac, m.p. 151—152°, and Bz derivative, m.p. 174.5—175°). *o*-C₆H₄Ph·OH (I) (Ac, m.p. 64°, and Bz derivative, m.p. 62°) yields similarly 2-hydroxydiphenyl-3-carboxylic acid (II) m.p. 186—187° [Ac, m.p. 128—129°, and Bz derivative, m.p. 118—118.5°; Me ether, m.p. 54—56°; Ph ether, m.p. 90—92°; anilide (III), m.p. 120—121°; *p*-toluidide (IV), m.p. 148—149°; *p*-chloroanilide, m.p. 155—156°]. Azo-dyes, obtained by coupling (II) with diazotised *p*-NO₂·C₆H₄·NH₂, *α*-C₁₀H₇·NH₂, and benzidine, and (III) and (IV) with *p*-NO₂·C₆H₄·N₂Cl, are described.

R. T.

Pyrenecarboxylic acids and ethylanilides.—See B., 1938, 1018.

Condensations by sodium. XIV. Phthalic acids and some factors influencing yields of butyl- and dimethyl-malonic acids. A. A. MORTON and F. FALLWELL, jun. (J. Amer. Chem. Soc., 1938, 60, 1924—1927; cf. A., 1938, II, 325).—In the C₆H₅-NaC₅H₁₁-CO₂ reaction *m*- and *p*-C₆H₄(CO₂H)₂ are formed from C₆H₄Na₂. Addition of NaC₅H₁₁ to

C_6H_6 and NaOBz and subsequent reaction with CO_2 gives $o-C_6H_4(CO_2H)_2$. Addition of NaOBz after formation of the NaPh increases the yield of $CPh_3\cdot OH$, but decreases that of $o-C_6H_4(CO_2H)_2$. Presence of Ni increases the yield of $CHBu(CO_2H)_2$ and (slightly) $o-C_6H_4(CO_2H)_2$, but not of $CMe_2(CO_2H)_2$. Adsorption of the various reactants on Na probably plays a part in controlling the direction of the reaction.

R. S. C.

Catalytic oxidation of naphthalene [to phthalic anhydride].—See B., 1938, 1018.

Polymerisation of phenylacetaldehyde. A. MÜLLER (Seifens.-Ztg., 1936, 63, 441—442; Chem. Zentr., 1936, ii, 3284; cf. A., 1934, 1301).—Polymerisation of $CH_2Ph\cdot CHO$ is considerable in diffuse autumn light (1 month) but is less in diffuse summer light than in the dark. Fixation of mobile electrons of the H atoms of the CH_2 in light of short λ is suggested rather than a polymerisation-depolymerisation equilibrium (cf. A., 1915, i, 261).

A. H. C.

Condensation of $\Delta^{\alpha\gamma}$ -butadiene with $\alpha\beta$ -unsaturated compounds. I. Synthesis of Δ^3 -tetrahydrobenzaldehyde, 6-methyl- Δ^3 -tetrahydrobenzaldehyde, and their derivatives. N. TSCHANJANOV (J. Gen. Chem. Russ., 1938, 8, 460—474).— Δ^3 -Tetrahydrobenzaldehyde (I) (*oxime*, b.p. 203—204°; *phenylhydrazone*, b.p. 207—208°/22 mm.; *p-nitrophenylhydrazone*, m.p. 163°; compound with NH_3 , m.p. 105—107°) is obtained in 90% yield from $(CH_2\cdot CH)_2$ and $CH_2\cdot CH\cdot CHO$ (30 min. at 150°), together with its trimeride, m.p. 175—176°. (I) and H_2O_2 yield a peroxide, $(CH\langle\begin{smallmatrix} CH-CH_2 \\ CH_2-CH_2 \end{smallmatrix}\rangle CH(OH)\cdot O)_2$, m.p. 90—91° (decomp.); in presence of H_2SO_4 and EtOH the product is *Et* Δ^3 -tetrahydrobenzoate, b.p. 194—195°. (I) in $COMe_2$ and aq. KOH yield 1:2:5:6-tetrahydrostyryl *Me* ketone, b.p. 118—120°/10 mm. (*semicarbazone*, m.p. 135—136°); the product with $COMeEt$ is γ -keto- β -methyl- Δ^{α} -butenyl-1:2:5:6-tetrahydrobenzene, b.p. 241—243°. $CHMe\cdot CH\cdot CHO$ and $(CH_2\cdot CH)_2$ (2 hr. at 160—180°) give 6-methyl- Δ^3 -tetrahydrobenzaldehyde (*semicarbazone*, m.p. 169—170°; *oxime*, m.p. 64.5—65.5°; *phenylhydrazone*, b.p. 211—212°; *p-nitrophenylhydrazone*, m.p. 173—174°), which with $COMe_2$ in aq. KOH gives 6-methyl-1:2:5:6-tetrahydrostyryl *Me* ketone, b.p. 245.5—246.5° (*semicarbazone*, m.p. 144—145°). R. T.

Nitrobenzaldehydes of the di- and poly-aryl ether series.—See B., 1938, 1018.

Attempted resolution of phenyl $\alpha\beta$ -dideuteroethyl ketone by an indirect method. J. B. M. COPPOCK, J. KENYON, and S. M. PARTRIDGE (J.C.S., 1938, 1069—1074).—The system CHDRR' does not appear to give rise to appreciable optical activity (cf. A., 1936, 840). (–)- α -Phenylallyl alcohol (I) (A., 1938, II, 275) with *p*-xenylcarbimide gives the (+)-*p*-xenylcarbamate, m.p. 134.8—135.2°, $[\alpha]_{D_{461}}^{20} +131.1^\circ$, which is reduced by D_2 (Adams) to (+)- α -phenyl- $\beta\gamma$ -dideutero-*n*-propyl *p*-xenylcarbamate (II), m.p. 137.9—138.4°, and by H_2 to (+)- α -phenyl-*n*-propyl *p*-xenylcarbamate (III), m.p. 138.3—138.7°; (II) and (III) have $[\alpha]_{D_{461}}^{20} +148.8^\circ$ and $+150.4^\circ$, respectively (all in C_6H_6). Attempts to resolve (II) by fractional crys-

tallisation are unsuccessful; more and less sol. crops show 'no difference in rotatory dispersion, and the slight differences in m.p. are also observed with (III). 3N-NaOH or -HCl does not hydrolyse (III), which with 30% (vol.) H_2SO_4 at 180° gives (*p*- $C_6H_4Ph\cdot NH_2$) $_2\cdot H_2SO_4$, unchanged (III), and a heavy oil. Reduction of (I) by D_2 gives phenyl- $\alpha\beta$ -dideuteroethylcarbinol (IV), of which the 3:5-dinitrobenzoate (recryst. thrice) had m.p. 52—53°, $[\alpha]_{D_{461}}^{20} -45.57^\circ$, and is hydrolysed (KOH-EtOH) to (IV), b.p. 207°, $\alpha_{D_{461}} +8.43^\circ$. This with CrO_3 -AcOH gives *Ph* $\alpha\beta$ -dideuteroethyl ketone (V), m.p. 19.5°, b.p. 208°, $\alpha_{D_{461}} \pm 0.01^\circ$, when regenerated from the semicarbazone, m.p. 175°, $\alpha \pm 0.01^\circ$ in AcOH or $COMe_2$. E. W. W.

Displacement of absorption bands of dyes with salt formation at the auxochrome groups. F. R. STORCK (Helv. Phys. Acta, 1936, 9, 437—466; Chem. Zentr., 1936, ii, 3782).—Quant. spectrographic examination of *p*-dimethylaminobenzylidene-acetophenone, -phenylacetone, and -acetone, and auramine, and their N^+ salts with HCl, H_2SO_4 , $HClO_4$, Me_2SO_4 , and MeI in H_2O or EtOH, shows that salt formation shifts the bands (extent depending on λ) towards the ultra-violet when the auxochrome is peripheral, and towards the red when central as in auramine. Dissociation of the pure solutions is so slight that the ionic contribution may be neglected.

A. H. C.

Condensation of *p*-dimethylaminobenzaldehyde with vanillylideneacetone and vanillylideneacetone derivatives. L. C. RAIFORD and M. M. COOPER (J. Org. Chem., 1938, 3, 11—15).—The appropriate aldehyde with $COMe_2$ in EtOH- $NaOH\cdot H_2O$ affords 2-, m.p. 133—134°, 5-, m.p. 143—144°, and 6-, m.p. 145.5—146.5°, -chloro-, and 2-bromo-, m.p. 139—140°, -vanillylideneacetone. Vanillylideneacetone with *p*- $NMe_2\cdot C_6H_4\cdot CHO$ (I) in EtOH- $NaOH\cdot H_2O$ gives 4'-dimethylamino-4-hydroxy-3-methoxydistyryl ketone, m.p. 199°, together with some di-*p*-dimethylaminostyryl ketone (II). 2-, m.p. 186—187°, 5-, m.p. 203—204°, and 6- (+0.5 H_2O), m.p. 95—110°, -chloro-, and 2-, m.p. 194—195°, 5-, m.p. 203—204°, and 6-, m.p. 185—185.5° (+0.5EtOH), m.p. 120—128° (decomp.), -bromo-4'-dimethylamino-4-hydroxy-3-methoxydistyryl ketones were similarly obtained, in most cases with larger amounts of (II). Better yields were obtained at room temp. than at 100° (bath), and when larger amounts of EtOH and NaOH than previously recommended were used. (II) is not formed by treating the foregoing mixed distyryl ketones with (I) under similar conditions. These derivatives are not formed from *p*- $NMe_2\cdot C_6H_4\cdot CH\cdot CH\cdot COMe$ and the appropriate vanillin derivative. H. G. M.

Synthesis of ketones from compounds of ethers with titanium tetrachloride. R. R. GALLE (J. Gen. Chem. Russ., 1938, 8, 402—409).—1- $C_{10}H_7\cdot OMe$ (I) with AcCl or BzCl in presence of $TiCl_4$ yields the corresponding 4-Ac or -Bz derivative; with 2- $C_{10}H_7\cdot OMe$ (II) the 1-Ac or -Bz derivative is obtained. (I), $(COCl)_2$, and $TiCl_4$ give a mixture of di-4-methoxy-1-naphthyl ketone and diketone, whilst with (II) the sole product is di-2-methoxy-1-naphthyl ketone. Thiophen, $(COCl)_2$, and $TiCl_4$ give di-2-thienyl ketone, and (largely) a stable Ti-containing

polymeric complex. $C_{10}H_7COR$ are not obtained from $C_{10}H_8$, $RCOCl$, and $TiCl_4$. R. T.

Preparation and reactions of magnesium 9-anthranyl bromide. W. E. BACHMANN and M. C. KLOETZEL (J. Org. Chem., 1938, 3, 55—61).—Mg 9-anthranyl bromide (I) is obtained in good yield when the pure bromide is refluxed in $Bu^a_2O-C_6H_6$ (12 hr.), Bu^a_2O (0.5 hr.), or (generally best) in Et_2O (24 hr.) with pure, pulverised Mg activated by I or (better) $EtBr$ (cf. Miller *et al.*, A., 1935, 741). In $Bu^a_2O-C_6H_6$ a *by-product*, m.p. 313—315°, sublimes at 250°/0.5 mm., was obtained. With I in Et_2O (I) gives 9-iodoanthracene, m.p. 82—83°, with MeI affords 9-methylanthracene, with CO_2 yields 9-anthracic acid in good yield, and with $PhCN$ gives *Ph anthranyl ketimine*, m.p. 152—153°, sublimes at 195°/0.5 mm. (*hydrochloride*, m.p. 272—274°), also obtained (in $Et_2O-C_6H_6$) from $MgPhBr$ and 9-cyanoanthracene, m.p. 174—175° [lit. 170—172°; prepared by heating the bromide with $Cu_2(CN)_2$ and C_5H_5N (220°, 9 hr.)], and hydrolysed with 36% HCl (sealed vessel, 145°, 80 hr.) to 9-benzoylanthracene. With $CHPh_2Br$ (I) in $Bu^a_2O-C_6H_6$ gives 9-benzhydrylanthracene, m.p. 204—205°, with $COPh_2$ affords *diphenylanthranylcarbinol*, m.p. 191—192°, and with fluorenone yields *anthranyldiphenylenecarbinol*, m.p. 205—206°. 9-Bromoanthracene (II) reacts readily with Li in anhyd. Et_2O giving Li anthranyl, converted by dil. HCl into anthracene (III). With maleic anhydride in boiling xylene (II) reacts more slowly than (III); the equilibrium favours formation of the adduct (94%) (cf. Barnett *et al.*, A., 1934, 1102).

H. G. M.

Synthesis of materials possessing the odour of jasmone. W. ISSAGULIANZ (Riechstoffind., 1936, 11, 84—86; Chem. Zentr., 1936, ii, 3373).— $Et_3methyl-n-amylbutanetricarboxylate$ (yield, 45%) gave tetrahydrojasmone (I) [*semicarbazone*, m.p. 142° (cf. Treff and Werner, A., 1933, 1296; 1935, 750; Ruzicka and Pfeiffer, A., 1934, 75)]. 3-Methyl-2-isoamylcyclopentanone, b.p. 98—99°/8 mm. (*semicarbazone*, m.p. 156—157°), prepared similarly, has a stronger odour than (I).

A. H. C.

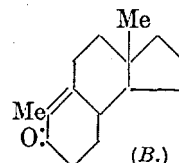
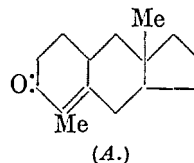
Condensation of acyclic aldehydes with cyclanolic ketones. Condensation of formaldehyde and acetaldehyde with cyclopentanone. H. GAULT and J. SKODA (Compt. rend., 1938, 207, 429—430; cf. A., 1923, i, 565).— CH_2O with an excess of cyclopentanone (I) at a low temp. in presence of K_2CO_3 affords 2-hydroxymethyl- (II), b.p. 94°/2 mm. (*phenylhydrazone*, m.p. 96—97°; *Ac* derivative, b.p. 120—121°/15 mm.), and 2:2-di(hydroxymethyl)-cyclopentanone (III), m.p. 25—27°, b.p. 146—148°/2 mm. (*phenylhydrazone*, m.p. 116—117°; *Ac_2* derivative, b.p. 169—170°/16 mm.). (II) and (III) with H_2 -Raney Ni afford 2-hydroxymethyl-, b.p. 137°/16 mm. (*Ac_2* derivative, b.p. 131°/18 mm.), and 2:2-di(hydroxymethyl)-cyclopentanol, undistillable (*Ac_2* derivative, b.p. 154—155°/5 mm.). (I) with $MeCHO$ similarly affords 2- α -hydroxyethylcyclopentanone, b.p. 95°/1 mm., and more complex products. $NaOH$ at room temp. converts (III) into a difficultly fusible insol. substance.

J. L. D.

Liquid-phase reactions at high pressures.
IV. Autocondensation of cyclohexanone, and its condensation with aniline. R. H. SAPIRO and S. P'ENG (J.C.S., 1938, 1171—1174; cf. A., 1937, I, 417).—Autocondensation of cyclohexanone (I) under pressure in absence of catalyst is studied further; the yield of 2- Δ^1 -cyclohexenylcyclohexanone (II) depends on temp. and pressure. Similar results are obtained with glass or SiO_2 tubes; the max. yields are 36.1 and 36.0%, respectively, at 100°/5000 atm. In presence of NH_2Ph , (I) affords its anil also, this being formed [but not (II)] even at 20°/1 atm. Both reactions are promoted by pressure, but they have opposite temp. coeffs. Yields of anils are recorded from equimol. mixtures of NH_2Ph and (I), its 2-Me derivative, cyclopentanone, and $COPhMe$ at 20—100° and 1 and 3500 atm. In absence of a condensing agent; $COMeEt$ and $COEt_2$ do not react. (I) and NH_2Ph at <100° and 5000 atm. afford, in addition, some anil of (II). A. T. P.

Synthesis of substances related to the sterols.

XX. Preparation of two tricyclic ketones. F. J. McQUILLIN and R. ROBINSON (J.C.S., 1938, 1097—1099).—*cis*-3(2)-Keto-9(10)-methyldecahydronaphthalene (A., 1937, II, 196; cf. *ibid.*, 413) with $NaNH_2$ in Et_2O and N_2 , followed by $COMe[CH_2]_2NMeEt_2I$ (I) in $EtOH$, gives 2-keto-11-methyl- $\Delta^{1:13}$ -dodecahydroanthracene, b.p. 149—151°/2 mm. (*semicarbazone*, m.p. 220°), which is dehydrogenated (Se at 360°) to anthracene. The crude condensation product from 2-methylcyclopentanone and (I) with $(NO_2)_2C_6H_3NHNH_2$ gives 2-methyl-2- γ -(ketobutyl)cyclopentanonebis-2:4-dinitrophenylhydrazone, m.p. 201°, and with $NaOEt-EtOH$ in Et_2O yields 5-keto-8-methyl- $\Delta^{4:9}$ -tetrahydrohydriene (A., 1937, II, 197), which is hydrogenated ($Pd-SrCO_3$) to 5-keto-8-methylhydriene, b.p. 110°/12 mm. (*semicarbazone*, m.p. 190°). This is oxidised by alkaline $KMnO_4$ to a dicarboxylic acid, $C_{10}H_{16}O_4$, m.p. 158°, and with $NaNH_2$ and $COEt[CH_2]_2NMeEt_2I$ as before gives a ketone (II), $C_{15}H_{22}O$, b.p. 189—191°/13 mm. (2:4-dinitrophenylhydrazone, m.p. 160°). (II) is probably (A) or (B)

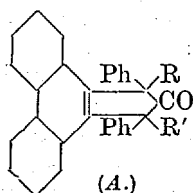
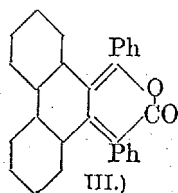


(which could be used to construct the α -cholesterol skeleton), and a hydrocarbon corresponding with (B), viz., 3'-methyl-4:5-benzhydryndene (III), m.p. 44° (*picrate*, m.p. 107°), has been synthesised (see below); (II) is, however, resistant to Se dehydrogenation, and identification is thus not possible. β -o-Tolylethyl chloride [the alcohol is obtained from $o-C_6H_4Me-MgBr$ and $(CH_3)_2O$] with Mg and cyclopentanone gives 1- β -o-tolylethylcyclopentan-1-ol, b.p. 141°/1 mm., converted by ice-cold 85% H_2SO_4 into 3'-methyl-6:7:8:9-tetrahydro-4:5-benzhydryndene, b.p. 97—99°/1 mm., dehydrogenated ($Pd-C$ at 340—360°) to (III).

E. W. W.

Heteropolarity. XXXIII. Oxidation and reduction products of phenyclone and acetylclone.

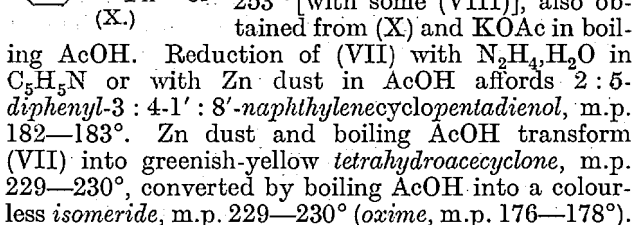
W. DILTHEY, S. HENKELS, and M. LEONHARD (J. pr. Chem., 1938, [ii], 151, 97—126).—Passage of air through a solution of phenacyclone (I) in C_5H_5N at 100° gives 9:10-dibenzoylphenanthrene (II), m.p. 206° , the constitution of which follows from its conversion by $N_2H_4 \cdot H_2O$ in cold C_5H_5N into 3:6-diphenyl-4:5-oo'-diphenylenepyridazine, m.p. 340° , by molten P_2S_5 into 2:5-diphenyl-3:4-oo'-diphenylenethiophen, m.p. 204° , and by Zn-Hg in AcOH into 2:5-diphenyl-3:4-oo'-diphenylenefuran, m.p. 184° . (II) differs from the 9:10-dibenzoylphenanthrene, m.p. 317° , obtained by Willgerodt and Albert (A., 1911, i, 882) from phenanthrene, $BzCl$, and $AlCl_3$ in CS_2 ; a repetition of this work gave only a dibenzoylphenanthrene, m.p. 184° . The mother-liquors from (II)



contain 3:6-diphenyl-4:5-oo'-diphenylene-2-pyrone (III), m.p. 273° , transformed by distillation with $NaOH-CaO$ into 9-benzylphenanthrene, m.p. 154° , identical with the product from phenanthrene and CH_2PhCl in presence or absence of Zn dust. Oxidation of (I) by H_2O_2 in $Ac_2O-AcOH$ gives mainly 2:5-diacetoxy-2:5-diphenyl-3:4-oo'-diphenylenecyclopentenone (IV) (A ; $R = R' = OAc$), m.p. 273° , also obtained by oxidation of (I) with $Pb(OAc)_4$ in AcOH, and together with a little (II). When heated or treated with conc. H_2SO_4 it is converted into (III). (IV) suspended in cold MeOH is transformed by HCl into 2:5-dichloro-2:5-diphenyl-3:4-oo'-diphenylenecyclopentenone (V) (A ; $R = R' = Cl$), m.p. 263° , also obtained from (I) and Cl_2 in addition to a second dichloride, m.p. 274° (probably *cis-trans* isomerides). PCl_5 transforms (I) in anhyd. C_6H_6 into a third dichloride, m.p. 278° . The m.p. of the chlorides diminish when they are preserved. They do not lose Cl in warm, indifferent solvents; with $AgOAc$ in AcOH they give (IV). In boiling AcOH (V) passes into 2:5-dihydroxy-2:5-diphenyl-3:4-oo'-diphenylenecyclopentenone (VI) (A ; $R = R' = OH$), m.p. $239-240^\circ$, transformed by conc. H_2SO_4 into (III), also obtained by cold Ac_2O and $NaOAc$ or by $AcCl$ and K_2CO_3 . Addition of Br to (I) in C_6H_6 affords 2:5-dibromo-2:5-diphenyl-3:4-oo'-diphenylenecyclopentenone (A ; $R = R' = Br$), m.p. 298° , transformed by boiling AcOH into (VI) and by $KOAc$ in AcOH into (IV). (I) and I in CH_2Cl_2 yield 2:5-di-iodo-2:5-diphenyl-3:4-oo'-diphenylenecyclopentenone, which immediately loses I in warm solvents and is converted by MeOH in $CHCl_3$ at room temp. into (III) accompanied by some (II); it is transformed by $KOAc$ in boiling AcOH into dihydrophenacyclone (A ; $R = R' = H$), m.p. 314° .

Accecyclone (VII) suspended in $PhCl$ is transformed by light and air into 7:8-dibenzoylacenaphthylene (VIII), m.p. $136-137^\circ$, whereas oxidation with BzO_2H in $PhCl$ leads only to yellow, resinous products. $N_2H_4 \cdot H_2O$ and (VIII) in EtOH give 2:5-diphenyl-

3:4-1':8'-naphthylenepyridazine (IX), m.p. $304-305^\circ$ (picrate, m.p. 238°). Reduction ($Zn-AcOH$) of (VIII) gives 7:8-dibenzoylacenaphthene, m.p. 176° , converted by $N_2H_4 \cdot H_2O$ into (IX). Treatment of (VII) with Cl_2 or PCl_5 in C_6H_6 yields dichlorodihydroaccecyclone (X), m.p. 198° (decomp.), converted by insolation in C_6H_6 into (?) (VIII). Oxidation of (VII) by H_2O_2 in AcOH affords 3:6-diphenyl-4:5-1':8'-naphthylene-2-pyrone, m.p. 253° [with some (VIII)], also obtained from (X) and $KOAc$ in boiling AcOH. Reduction of (VII) with $N_2H_4 \cdot H_2O$ in C_5H_5N or with Zn dust in AcOH affords 2:5-diphenyl-3:4-1':8'-naphthylenecyclopentadienol, m.p. $182-183^\circ$. Zn dust and boiling AcOH transform (VII) into greenish-yellow tetrahydroaccecyclone, m.p. $229-230^\circ$, converted by boiling AcOH into a colourless isomeride, m.p. $229-230^\circ$ (oxime, m.p. $176-178^\circ$).



H. W.
Higher aromatic keto-fatty acids.—See B., 1938, 1016.

Syntheses in the pinane group. IV. Attempted synthesis of pinonic acid. Synthesis of *trans*-2:2-dimethyl-3-acetoncyclobutane-1-carboxylic acid. Constitution of Fujita's keto-carboxylic acid, $C_{10}H_{16}O_3$. Syntheses of nopinone and verbenone. P. C. GUHA and P. L. N. RAO (Ber., 1938, 71, [B], 1591—1595).—Largely a more detailed account of work previously abstracted (A., 1938, II, 283). The following appears new. Addition of EtOH (1 mol.) to pinyl dichloride in light petroleum affords a little *Et trans*-3-carboxy-2:2-dimethylcyclobutylacetate, b.p. $161-162^\circ/5$ mm., $210-215^\circ/15$ mm. Norpinsemialdehyde condenses with $CH_2(CO_2H)_2$ to β -3-carboxy-2:2-dimethylcyclobutyl-acrylic acid, which is reduced to the -propionic acid. Norpinyl dichloride appears to be transformed by $ZnMeI$ under defined conditions into a diketone, m.p. $103-105^\circ$, which may be capable of transformation into verbenone. *trans*-3-Carbethoxy-2:2-dimethylcyclobutylacetamide and -anilide have m.p. 97° and b.p. $218-220^\circ$ (slight decomp.)/3 mm., respectively.

H. W.

Function of the cyano-group in tautomeric systems. F. ARNDT and L. LOEWE [with Z. GÜNTHER and F. SIPAHİ] (Ber., 1938, 71, [B], 1627—1630).—The electromeric effect of CN is approx. the same as that of CO_2Alk . $CHCl_2 \cdot CO \cdot NH_2$, $NaOMe$, and p - $C_6H_4Me \cdot SH$ in MeOH yield *di*-*p*-tolylthiolacetamide (I), m.p. 175° after softening, oxidised by H_2O_2 in AcOH to *di*-*p*-toluenesulphonylacetamide, m.p. 195° (decomp.), which does not give a colour with $FeCl_3$ in EtOH. (I) is transformed by P_2O_5 in boiling C_6H_6 followed by H_2O_2-AcOH into *di*-*p*-toluenesulphonyl-acetonitrile, m.p. 160° , readily sol. in alkali hydroxide and warm $2N-Na_2CO_3$ and giving a brownish-pink colour with $FeCl_3$ in EtOH. The violent reaction with CH_2N_2 does not lead to a cryst. product. Reproducible enol vals. are obtained when the equilibrium solution of $CH_2Bz \cdot CN$ in EtOH at -15° is very rapidly treated with Br , the excess of which is immediately removed by β - $C_{10}H_7 \cdot OH$. The val. is about one third < that of $CH_2Bz \cdot CO_2Et$. In EtOH it does not give a

colour with FeCl_3 , indicating the presence of the enol exclusively in the *trans* form, $\text{N:C-CH} \begin{smallmatrix} \text{CPh-OH} \\ \text{N:C-CH} \end{smallmatrix}$.

H. W.

Condensations brought about by bases. III. General course of the Claisen type of condensation. C. R. HAUSER. IV. Condensation of ethyl isobutyrate with benzoyl chloride, benzoic anhydride, and phenyl benzoate as examples of the Claisen type of condensation. B. E. HUDSON, jun., R. H. DICK, and C. R. HAUSER (J. Amer. Chem. Soc., 1937, 60, 1957—1959, 1960—1962; cf. A., 1938, II, 143).—III. All condensations of an enolate ion with compounds containing RCO by bases to give $\alpha\gamma$ -diketones are classed as Claisen-type condensations. The mechanism of the reactions is discussed.

IV. When $\text{Pr}^i\text{CO}_2\text{Et}$ is added to CPh_3Na (prep. described) in Et_2O and shortly thereafter treated with BzCl , Bz_2O , or PhOBz , 50—55% yields of $\text{CMe}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ are formed. EtOAc and CPh_3Na give 43% of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ in 3 min.; addition of EtOBz gives also a little $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$. Addition first of EtCO_2Et and then of BzCl to CPh_3Na gives only high-boiling products, but simultaneous addition of EtCO_2Et and PhOBz to CPh_3Na gives a poor yield of $\text{CHMeBz}\cdot\text{CO}_2\text{Et}$. $\text{EtOAc}\cdot\text{EtOBz}$ and $\text{EtCO}_2\text{Et}\cdot\text{EtOBz}$ give low yields of $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ and $\text{CHMeBz}\cdot\text{CO}_2\text{Et}$, respectively. These reactions are considered to be Claisen-type condensations.

R. S. C.

Interaction between anthracene and succinic anhydride. E. BERGMANN and A. WEIZMANN (J.C.S., 1938, 1243—1244).—1'-Keto-1':2':3':4'-tetrahydro-1:2-benzanthracene is prepared in similar manner to that described by Cook and Robinson (A., 1938, II, 227), who accord priority for the synthesis of 1'-methyl-1:2-benzanthracene to Fieser and Peters (A., 1933, 67). The orientation of β -2-anthroyl-propionic acid (I) (*Et* ester, m.p. 138—140°) is proved by synthesis. 2-Acetylanthracene and Br in Et_2O at 0° give 2-bromoacetylanthracene (II), m.p. 155°; excess of Br yields a Br_2 -compound, m.p. 162° (? 9:10-dibromo-2-bromoacetyl-9:10-dihydroanthracene). $\text{CHNa}(\text{CO}_2\text{Et})_2$ and (II) form a product, converted by $\text{KOH}\cdot\text{MeOH}$ into (I). In preparing (I) from anthracene and $(\text{CH}_2\text{CO})_2\text{O}$ some β -1-anthroyl-propionic acid, m.p. 125°, is obtained. Anthracene, $\text{CH}_2\text{Cl}\cdot\text{COCl}$, and AlCl_3 in $\text{C}_6\text{H}_5\text{Cl}_4$ at 0° form a bis-chloroacetylanthracene, m.p. 205°. A. T. P.

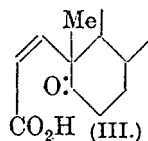
Phenacyl and *p*-substituted phenacyl esters. R. V. LUNDQUIST (J. Amer. Chem. Soc., 1938, 60, 2000).—Phenacyl heptoate, dichloroacetate, and α -bromo-*n*-butyrate, oils, and acetylsalicylate, m.p. 105—105.5°, *p*-bromo-, m.p. 98.2—98.3°, and *p*-chlorophenacyl dichloroacetate, m.p. 93—93.8°, and *p*-phenylphenacyl α -bromo-*n*-butyrate, m.p. 103.5—104°, are prepared. R. S. C.

Reaction of iodine monobromide with cholestenone and β -cholestanone. J. O. RALLS (J. Amer. Chem. Soc., 1938, 60, 1744—1753).—The reaction of cholestenone (I) and cholestanone (II) with IBr is autocatalytic. These reactions and that of 2

bromocholestanone (III) are of the first order and are catalysed by HBr ; moderate amounts of HBr decrease the total amount of halogen absorbed, but increase that organically bound. Br is the active ingredient of IBr . The catalytic effect of HBr is due to its increasing the enolisation of the ketone; the effect of larger amounts is due to some interference in the complex series of reactions. The ethylenic linking of (I) has no part in the reaction, as the oximes of (I) and (II) do not react. With IBr (II) gives mainly (III), m.p. 171.5°, with small amounts of Br_2 -derivatives, (IV), m.p. 147°, and (V), m.p. 194°. (III) is unaffected by hot $\text{C}_5\text{H}_5\text{N}$. With IBr (III) gives (IV), proving the latter to be a 2: α - Br_2 -derivative. (V) is probably a 2:4- Br_2 -derivative; with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ it gives the *o*-aminoanil, m.p. 184°. With KOAc in $\text{EtOH}\cdot\text{C}_6\text{H}_6$ (IV) gives a compound, m.p. 119°, and (V) gives a mixture, in which, however, a diosphenol could not be recognised. R. S. C.

Transformations of brominated derivatives of cholesterol. V. Experiments with dibromocholestanone. H. H. INHOFFEN and HUANG-MIN-LON (Ber., 1938, 71, [B], 1720—1730; cf. A., 1937, II, 423).—The action of $\text{C}_5\text{H}_5\text{N}$ on 2:4-dibromocholestanone (I) at 135° gives a mixture of products from which $\Delta^{1:2:4:5}$ -cholestadien-3-one (II), m.p. 111.5—112.5°, $[\alpha]_D^{25} + 28.1^\circ$ in CHCl_3 (semicarbazone, m.p. 230—231°), is isolated. Hydrogenation (Pd sponge in Et_2O) of (II) yields coprostanone whereas partial ozonisation affords the acid, $\text{C}_{26}\text{H}_{42}\text{O}_3$ (III), m.p. 207—207.5°, the structure of which is established by its absorption spectrum and its instability towards KMnO_4 . Partial hydrogenation (Rupe's Ni in EtOH) of (II) yields $\Delta^{1:2}$ -coprosten-3-one, m.p. 81—83° (clear at 85°), $[\alpha]_D^{25} + 64.6^\circ$ in CHCl_3 (semicarbazone, m.p. 207°), the spectrum of which shows that it is an $\alpha\beta$ -unsaturated ketone. (I) is reduced by $\text{Al}(\text{OPr}^i)_3$ in boiling $\text{C}_6\text{H}_6\text{-Pr}^i\text{OH}$ to 2:4-dibromocholestan-3-ol, m.p. 174—175° (acetate, m.p. 178—179°). This is unchanged by prolonged boiling with $\text{C}_5\text{H}_5\text{N}$ even in presence of AgNO_3 or by KOBz in $\text{Bu}^i\text{CO}_2\text{H}$ but is transformed by KOBz in BzOH at 220° into 2-benzoyloxycholestan-3-one (IV), m.p. 198—199°, also obtained [together with an isomeric benzoate (V), m.p. 145—146°] from 2-bromocholestanone and KOBz in boiling $\text{Bu}^i\text{OH}\cdot\text{PhMe}$. Mild hydrolysis ($\text{KOH}\cdot\text{EtOH}\cdot\text{C}_6\text{H}_6$ at room temp.) of (IV) affords 2-hydroxycholestan-3-one, m.p. 125—127° after softening, reconverted (BzCl in $\text{C}_5\text{H}_5\text{N}$) into (IV) whereas $\text{KOH}\cdot\text{MeOH}$ in presence of H_2O_2 transforms (IV) into the previously described (*loc. cit.*) dicarboxylic acid (VI), m.p. 195—196°, also obtained similarly from (V). In the absence of H_2O_2 (IV) and (V) are converted by $\text{KOH}\cdot\text{MeOH}$ into cholestane-2:3-dione, m.p. 161—162°, and (VI). H. W.

Conversion of *trans*-dehydroandrosterone into pregnane derivatives. L. RUZICKA and H. F. MELDAHL (Nature, 1938, 142, 399).— Δ^5 -17-Ethynyl-androstene-3-*trans*-17-diol (I) (A., 1937, II, 505) and AcOH in presence of Ac_2O , HgO , and $\text{BF}_3\cdot\text{Et}_2\text{O}$ give Δ^5 -20-acetoxypregnadiene-3-*trans*-17-diol (II), m.p. 175—177° (corr.). The 3-monoacetate of (I) also



adds AcOH forming $\Delta^5:20$ -3-*trans*-20-diacetoxypregnadien-17-ol (III), m.p. 191—192° (corr.). Alkaline hydrolysis of (II) or (III) yields Δ^5 -pregnene-3-*trans*-17-diol-20-one, m.p. 275—277° (corr.), $[\alpha]_D^{25}$ -78° in dioxan [oxime, m.p. 245—247° (corr.); 3-monoacetate (Ac₂O and C₅H₅N in the cold), m.p. 270—272° (corr.)].
L. S. T.

Δ^1 -Androsten-17-ol-3-one, an isomeride of testosterone. A. BUTENANDT and H. DANNENBERG (Ber., 1938, 71, [B], 1681—1685).—Androstan-17-ol-3-one acetate in AcOH containing HBr is transformed by Br-AcOH at 20° into 2-bromoandrostan-17-ol-3-one acetate (I), m.p. 177—178°, hydrolysed by HCl-MeOH at room temp. to 2-bromoandrostan-17-ol-3-one (II), m.p. 181° (decomp.). From the products of the action of KOAc in AcOH on (I) or (II) at 200° the *oxime*, m.p. 213—215° (decomp.), of (III) (below) is isolated in very small yield with, in the case of (II), a *product*, (?) C₂₁H₂₈O₃, m.p. 208°. Addition of Δ^1 -androstene-3:17-dione in EtOH to fructose undergoing fermentation by baker's yeast gives (83% yield) Δ^1 -androsten-17-ol-3-one, m.p. 158—159°, $[\alpha]_D^{25}$ -42.3° in EtOH [acetate (III), m.p. 118—119°], which has pronounced oestrogenic properties.
H. W.

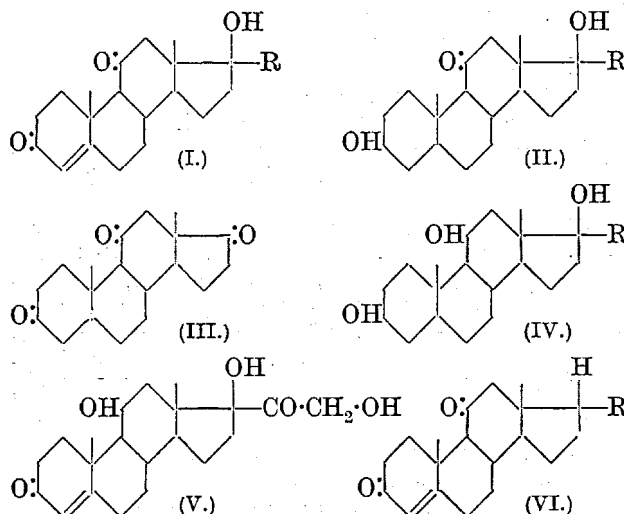
Acetalising reactions with steroid ketones; new method of preparing testosterone and dihydrotestosterone. A. SERINI and H. KÖSTER (Ber., 1938, 71, [B], 1766—1770).—Cholestanone (I), CH(OEt)₃, and EtOH-HCl in C₆H₆ at 70° afford *cholestanone Et₂ acetal*, m.p. 68—69.5°, $[\alpha]_D^{25}$ +26° in dioxan, hydrolysed by boiling dil. HCl to (I) and converted in boiling xylene into *cholestanone-enol Et ether*, m.p. 87—88°, $[\alpha]_D^{25}$ +63.1° in dioxan, hydrolysed to (I); the change is :C(OEt)₂ → >C·OEt + EtOH. Similarly, androstane-3:17-dione (II) affords *androstane-3:17-dione 3-Et₂ acetal* (III), m.p. 121—123°, $[\alpha]_D^{25}$ +75.6° in dioxan, hydrolysed to (II) and passing in boiling xylene into *androstane-3:17-dione-3-enol Et ether*, m.p. 105—106°, $[\alpha]_D^{25}$ +126° in dioxan. Reduction (Na in Pr^oOH) of (III) affords dihydrotestosterone, m.p. 176—177°, $[\alpha]_D^{25}$ +32° in EtOH. Androstene-3:17-dione (IV) (in C₆H₆), CH(OEt)₃, and EtOH-HCl at 75° yield directly *androstene-3:17-dione-3-enol Et ether*, m.p. 152°, $[\alpha]_D^{25}$ -89° in dioxan, hydrolysed by acid to (IV); it is also obtained from (IV) and CMe₂(OEt)₂ and is reduced (Na and Pr^oOH) to testosterone-enol Et ether, m.p. 118—122°, which is hydrolysed to testosterone. Under somewhat different conditions (IV) and CH(OEt)₃ yield *androstene-3:17-dione-3-enol Et ether 17-Et₂ acetal*, m.p. 91—92.5°, $[\alpha]_D^{25}$ +141.6° in dioxan, hydrolysed to (IV).
H. W.

Highly active esters of testosterone. K. MIESCHER, A. WETTSTEIN, and E. TSOHOFF (Schweiz. med. Woch., 1936, 66, 763—764; Chem. Zentr., 1936, ii, 3427).—Esters with fatty acids C₁₋₁₈ are described. In the capon test, esters of acids C₁₋₃ are equiv., higher esters having a more protracted but less intense action whilst in the rat test the propionate is the most active; lower esters are also active but the activity decreases rapidly with an increasing C chain. The possible ester character of the natural hormone is discussed and *esters* with the follow-

ing acids are described: HCO₂H, m.p. 127—129°; AcOH, m.p. 140—142°; EtCO₂H, m.p. 121—123°; Pr^oCO₂H, m.p. 111—113°; Pr^oCO₂H, m.p. 134—136°; Bu^oCO₂H, m.p. 109—111°; Bu^oCO₂H, m.p. 138—140°; deoic, m.p. 55—57°; palmitic, m.p. 72—74°; stearic, m.p. 79—80°; BzOH, m.p. 198—200°.
A. H. C.

Biochemical dehydrogenation in the testicular hormone series; bacterial oxidation of dehydroandrosterone to androstenedione. L. MAMOLI and A. VERCELLONE (Ber., 1938, 71, [B], 1686—1687).—Previous results (A., 1938, II, 103, 104) could not be repeated. Since aerobic bacteria cultivated in an impoverished yeast prep. are able to dehydrogenate dehydroandrosterone to Δ^4 -androstenedione in excellent yield, it is probable that the dehydrogenation observed previously (*loc. cit.*) is due entirely to the presence of such micro-organisms.
H. W.

Adrenal cortex. IV. Structures of compounds C, D, E, F, and G. H. L. MASON, W. M. HOEHN, and E. C. KENDALL. V. Conversion of compound E into the series which contains four atoms of oxygen and into adrenosterone by the action of calcium hydroxide. H. L. MASON (J. Biol. Chem., 1938, 124, 459—474, 475—479).—IV. Reichstein's formula (A., 1937, II, 506; cf. also A., 1936, 1382) for compound-E (his Fa), i.e., (I) (R = CO·CH₂·OH), is adopted. The HIO₄ oxidation product of E, acid-5 (A., 1937, II, 25), now formulated as (I) (R = CO₂H) (the ethylenic linking does not react with BzO₂H), is converted (C₅H₅N-Ac₂O) into its Ac₁ derivative, m.p. 239—243°, $[\alpha]_{D_{461}}^{25}$ +118.5±1.9° in EtOH (2:4-dinitrophenylhydrazone); as this is recryst. unchanged from aq. media it cannot be an easily hydrolysed enol acetate, and enolisation of the 3-CO group is thus excluded. With H₂ + PtO₂ and N-NaOH in EtOH, acid-5 gives *acid-5B* (II) (R = CO₂H), m.p. 290—293°, $[\alpha]_{D_{461}}^{25}$ +42.5±2°, and an isomeric acid, C₂₀H₃₀O₅, m.p. 283—287°, respectively pptd. and not pptd. by digitonin. Further hydrogenation is indefinite. Residual material after hydro-



genation is oxidised (K₂Cr₂O₇-H₂SO₄ in COMe₂) to ketone-3 (III), m.p. 179—181°, $[\alpha]_{D_{461}}^{25}$ +191±1.5° in

EtOH. The position of the fifth O in *E* is uncertain; it is assigned to C₁₁ on account of its inertness; thus acid-5B does not react with 2:4-(NO₂)₂C₆H₃·NH·NH₂ or MgMeI, and its Ac₂ derivative, m.p. 259–260°, [α]_D²⁵₄₆₁ –25.6±1.8° in EtOH, is not oxidised by CrO₃–AcOH. Compound-*C* (Reichstein's *C*), now formulated as (IV) (R = CO·CH₂·OH) (cf. A., 1937, II, 506–507), is oxidised by HIO₄ to CH₂O and an acid (IV) (R = CO₂H), m.p. 240–243°, [α]_D²⁵₄₆₁ +32.8±3.3° in EtOH, pptd. by digitonin. The oxidation product from acid-3 is not C₂₀H₃₀O₃ (A., 1936, 1117), but (III). Compound-*D* (Reichstein's *A*), now formulated as (IV) [R = CH(OH)·CH₂·OH], m.p. (+H₂O) 160–164° (uncorr.), m.p. (anhyd.) 165–167° [Reichstein's solidification and remelting (A., 1936, 473) not observed], is oxidised to impure (III), m.p. 160–161.5°. Aq. residues after removal of *E* contain compound-*F* (Reichstein's *M*; cf. A., 1937, II, 506) (V), m.p. 217–220°, [α]_D²⁵₄₆₁ +178°±2° (in EtOH?), converted by HIO₄ into CH₂O and an acid, C₂₀H₂₈O₅, m.p. 228–238°, and further by CrO₃ into ketone-4 (Reichstein's *G* or adrenosterone) (which the authors have not detected in cortex extracts). The liberation of 1 CH₄ by the last from MgMeI is attributed to enolisation of the hindered CO at C₁₁, not of that at C₃ (cf. acids 5 and 5A above). Compound-*G* (Reichstein's *D*), m.p. 228–236° (uncorr.), [α]_D²⁵₄₆₁ +83°±2° in EtOH, now formulated as (II) (R = CO·CH₂·OH), from fraction II, is oxidised by HIO₄ to acid-5B and CH₂O. *E* has about 1/5 the physiological activity of corticosterone. M.p. are corr. except where stated; m.p. >200° are with decomp.

V. Conversion from the C₂₁O₅ into the C₂₁O₄ series is effected. Compound-*E* (in EtOH) with saturated aq. Ca(OH)₂ in N₂ gives adrenosterone and acidic material. The latter with K₂Cr₂O₇–H₂SO₄–COMe₃ gives acid-1 (VI) (R = CO₂H) (cf. A., 1937, II, 459) [also obtained by oxidation of compound-*A* (VI) (R = CO·CH₂·OH)] and adrenosterone. *E* is 17-hydroxy-*A*. The possibility that acid-1 is derived from *A* or *B* (corticosterone; 11-dihydro-*A*), present as impurity in *E*, is excluded by the failure to obtain acid-1 from the *E* used and HIO₄ followed by CrO₃. *B* is unaffected by Ca(OH)₂. E. W. W.

Fission and fractionation of "corticosterone." M. PICCININI (Boll. Chim. farm., 1938, 77, 489).—The following substances were isolated: *A*, C₂₁H₂₅O₄, m.p. 174–181.5°; *B*, C₂₁H₃₀O₄, m.p. 177–179° (physiologically active and identical with corticosterone); *C*, C₂₁H₃₄O₅, m.p. 245–250°; *F*, C₂₁H₃₀O₅, m.p. 214–220°; *G*, C₂₁H₃₂O₅, m.p. 228–238°. *A* and *B* are oxidised (HIO₄) to CH₂O and the acid C₂₀H₂₆O₄, m.p. 258–260°, and C₂₀H₂₈O₄, m.p. 255–258°, respectively. *C* and *G* are Reichstein's *C* and *D*, respectively (A., 1937, II, 506). Reactions indicating the groups present in some of the above substances are briefly described. F. O. H.

Sterols. XL. Origin and interrelationships of the steroidal hormones. R. E. MARKER (J. Amer. Chem. Soc., 1938, 60, 1725–1736; cf. A., 1938, II, 369).—Reasons are advanced against the view that steroidal hormones and bile acids are derived

from cholesterol, notably the difficulty of introducing O into the ring-system and of oxidising the side-chain. Schemes are detailed, whereby the pregnane, androstane, and urane derivatives of C₁₈, C₁₉, and C₂₁ types and the sterols in the cortical extract are derived according to definite rules from the common precursor, $\Delta^1:8$ -pregnadiene-17:21-diol-3:11:20-trione (I) or its hydrate at C₉. Most of the proposed changes have counterparts in the laboratory. The rules account for all the products isolated and predict the occurrence of some more and absence of others. R. S. C.

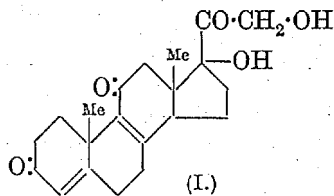
Leptospermone. I. L. H. BRIGGS, A. R. PENFOLD, and W. F. SHORT (J.C.S., 1938, 1193–1196; cf. B., 1926, 511).—"Leptospermol" is not a monobasic acid but is a β -diketone belonging to the same group as angustione and dehydroangustione (A., 1931, 487) and the authors rename it *leptospermone* (I), C₁₅H₂₂O₄. (I) has b.p. 146°/10 mm.; contains 2 active H, gives an *anilino*-derivative, C₂₁H₂₇O₃N, m.p. 91°, acryst. Cu salt, and an *anhydrophenylylhydrazone* (II), m.p. 118°, containing a pyrazole ring. (I) and HNO₃–H₂SO₄ at 50° gives CMe₂(CO₂H)₂ only, whilst KMnO₄ at <45° affords COPr₂ and CH₂Pr ^{β} ·CO₂H. (I) and (II) are probably 2-isovaleryl-4:4:6:6-tetramethylcyclohexane-1:3:5-trione and CMe₂·CMe₂·C·NPh CMe₂·CO·C·CBu ^{δ} >>N, respectively. A. T. P.

Semiquinone radicals in the indamine and indophenol groups.—See A., 1938, I, 521.

Compounds from aminoanthraquinones and $\alpha\beta$ -unsaturated carbonyl compounds.—See B., 1938, 1019.

1:3-Dihalogeno-2-methylaminoanthraquinones.—See B., 1938, 1018.

Synthetic experiments in the rubrene series. E. BERGMANN (J.C.S., 1938, 1147–1150; cf. A., 1936, 992, 1499).—1:2-Diphenylisobenzfuran (I) and maleic anhydride form an adduct (II), converted by HCl–MeOH (followed by MeOH–KOH), or better by HBr–AcOH at 37° for 2 days, into 1:4-diphenyl-naphthalene-2:3-dicarboxylic anhydride (III), m.p. 273–275° [free acid, m.p. 295° (decomp.) (*Bu* H ester, m.p. 238°)]. (II) and HCl–MeOH at 0°, followed by MeOH–KOH and then SOCl₂, give also a *dilactone* m.p. 250–252° (probably the *di- γ -lactone* of 1:4-dihydroxy-1:4-diphenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic acid). (III) and MgPhBr afford a keto-acid, cyclised by BzCl in 1-C₁₀H₇Cl into 6:11-diphenyl-naphthacene-5:12-quinone (IV), m.p. 282°. The use of conc. H₂SO₄ at room temp. as dehydrating agent yields (?) 6:11-dihydroxy-6:11-diphenyl-6:11-dihydronaphthacene-5:12-quinone, m.p. >360°. (IV) is obtained more readily from the adduct, yellow, m.p. 150° (reddish-black liquid), of (I) and α -naphthaquinone in xylene, and 40% HBr in AcOH at 37° for 2 days, 5:12-dihydroxy-6:11-oxido-6:11-diphenyl-naphthacene (?), m.p. 150°, also being formed. 1-Phenylnaphthalene-2:3-dicarboxylic anhydride and



MgPhBr in PhMe form a keto-acid, converted by conc. H_2SO_4 at room temp. for 20 hr. into 5-phenyl-naphthacene-6:11-quinone, m.p. 215°, which with LiPh takes up one Ph only, to form (?) 11-hydroxy-6-keto-5:11-diphenyl-6:11-dihydronaphthacene, m.p. 248° (decomp.). Naphthacenediquinone and LiPh give no phenylated product, only dihydroxy-naphthacenequinone being isolated. A. T. P.

Action of acetic anhydride on α -pinene in presence of boric acid. I, II. M. IMOTO (J. Soc. Chem. Ind. Japan, 1938, 41, 209—212B; cf. Schmidt, B., 1925, 229).—I. *l*- α -Pinene (I), Ac_2O , and B_2O_3 , heated at 220—95° for 14 hr., give unchanged oil, camphene, dipentene, limonene, and esters (22% yield) hydrolysed to borneol and isoborneol and fenchyl alcohol. *l*- and *d*- α -Pinene, Ac_2O , and cryst. H_3BO_3 in different proportions at 110—150° afford a larger yield of esters (37—58%).

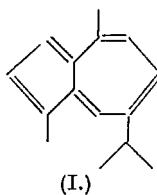
II. A more detailed fractionation of the products of the latter reaction with (I) indicates the presence of all the above reaction compounds, together with *p*-cymene, some polymerised substance, and an unknown alcohol, $\text{C}_{10}\text{H}_{17}\text{OH}$ (*H phthalate*, m.p. 162—163°). A. T. P.

Caryophyllenes. VI. γ -Caryophyllene. G. R. RAMAGE and J. L. SIMONSEN. VII. Experiments on the synthesis of caryophyllenic acid. M. D. OWEN, G. R. RAMAGE, and J. L. SIMONSEN (J.C.S., 1208—1211, 1211—1214).—VI. γ -Caryophyllene α -nitrosochloride and $\text{C}_5\text{H}_5\text{N}$ give oximino- γ -caryophyllene, b.p. 162—167°/5 mm., reduced (Na-EtOH) to aminodihydro- γ -caryophyllene (I), b.p. 147°/13 mm., the Ac derivative of which on ozonolysis affords CH_2O and a ketone (II), $\text{C}_{16}\text{H}_{27}\text{O}_2\text{N}$, m.p. 139—140°, $[\alpha]_{5461}^{20} -58^\circ$ in EtOAc. Hydrogenation of (I) yields aminotetrahydro- γ -caryophyllene, b.p. 147°/11 mm., which is deaminated and dehydrated to dihydro- γ -caryophyllene, b.p. 140°/24 mm., $\alpha_{5461}^{20} -26.1^\circ$, oxidised (O_3) to a liquid keto-acid, $\text{C}_{15}\text{H}_{26}\text{O}_3$ (*Ag salt*). Ozonolysis of acetamido- β -caryophyllene gives CH_2O and (II). It is suggested that β - and γ -caryophyllene are stereoisomerides.

VII. $\text{CMe}_2(\text{CH}_2\text{OAc})_2$ and HBr give $\text{CMe}_2(\text{CH}_2\text{Br})_2$ and the α -bromo- γ -acetoxy-compound, b.p. 85—95°/26 mm. The Br_2 -compound and Et potassiumalonate afford *Et* 3:3-dimethylcyclobutane-1:1-dicarboxylate, b.p. 118—119°/20 mm., hydrolysed to the acid, decomp. 162°, which is decarboxylated to 3:3-dimethylcyclobutanecarboxylic acid (III), b.p. 204°/760 mm. (*p*-phenacyl ester, m.p. 92°). The acid and SOCl_2 , followed by Br and MeOH, yield *Me* 1-bromo-3:3-dimethylcyclobutane-1-carboxylate, b.p. 82—83°/14 mm. Debromination with NPhEt_2 gives *Me* 3:3-dimethylcyclobutanecarboxylate, b.p. 70—80°/30 mm., and with KOH, 1-hydroxy-3:3-dimethylcyclobutane-1-carboxylic acid, m.p. 83°, is obtained. CMe_2CO and CH_3N_2 give 3:3-dimethylcyclobutanone (IV), b.p. 122—124°/770 mm. (*semicarbazone*, m.p. 234°). It is proposed to use (III) and (IV) for the synthesis of caryophyllenic acid. F. R. S.

Aromadendrene. II. C. B. RADCLIFFE and W. F. SHORT (J.C.S., 1938, 1200—1203).—Aromadendrene (I), obtained from *Eucalyptus rariflora* (30% yield) and *E. globulus* (37% yield), has m.p. 84.5—

85°, $[\alpha]_{5770}^{17} +5.75^\circ$ in EtOH, and forms α -, m.p. 195—196° (decomp.), and β -semicarbazones, m.p. 201.5—202.5° (decomp.), a *p*-nitrophenylhydrazones, m.p. 131°, and a benzylidene derivative, m.p. 66—66.5°. Reduction (Na) of (I) gives aromadendrol, b.p. 139—140°/10 mm., m.p. 54—59°, and of the oxime of (I) affords aromadendrylamine (*H oxalate*, m.p. 164—165°). With KMnO_4 aromadendrene gives (I), aromadendrene glycol, m.p. 118°, and an acid, m.p. 175—176° (decomp.). Dehydrogenation (S) of aromadendrene gives *S*-guaiazulene in 6.3% yield. The provisional formula for (I) is suggested. F. R. S.



Structure of triterpenes and related substances.—See A., 1938, I, 502.

Uncertain principles of lignin chemistry? E. WEDEKIND (Zellstoff-Faser, 1936, 33, 14—15; Chem. Zentr., 1936, ii, 3679).—Treatment of beechwood alternately with Schweitzer's reagent and $\text{H}_2\text{C}_2\text{O}_4$ yields a product identical with Storch's beechwood lignin (A., 1936, 207) which is thus, contrary to Hilpert (cf. A., 1935, 550), not a reaction product of carbohydrate origin. A. H. C.

Resinols. V. β -Amyrenol and dehydro- β -amyrenol. Location of the unsaturated centres of the α - and β -amyrenols. J. H. BEYNON, K. S. SHARPLES, and F. S. SPRING (J.C.S., 1938, 1233—1236).—Oxidation (CrO_3) of β -amyrenyl benzoate gives β -amyrenonyl benzoate, m.p. 265°, $[\alpha]_{575}^{25} +126.6^\circ$ in CHCl_3 , hydrolysed to β -amyrenonol (I), m.p. 175°, $[\alpha]_{575}^{25} +113.2^\circ$ in CHCl_3 . β -Amyrenonyl acetate, m.p. 260—261°, $[\alpha]_{575}^{25} +157.9^\circ$ in CHCl_3 , is reduced (Pd-H_2) to β -amyrenyl acetate. Reduction ($\text{Na-C}_5\text{H}_{11}\text{OH}$) of (I) yields a product, $\text{C}_{30}\text{H}_{50}\text{O}_2$, EtOH, m.p. 220—221°, which with Ac_2O gives dehydro- β -amyrenyl acetate, m.p. 208—209°, $[\alpha]_{575}^{25} +331^\circ$ in CHCl_3 . Oxidation (CrO_3) of dehydro- α -amyrenyl acetate affords an acetate, $\text{C}_{32}\text{H}_{50}\text{O}_4$, m.p. 312°, $[\alpha]_{575}^{25} +61.1^\circ$ in CHCl_3 . Light absorption data are given and the structures of the α - and β -amyrenols are discussed. F. R. S.

Toad venom. VIII. Structure of γ -bufotalin. M. KOTAKE and T. KUBOTA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 824—831).—EtOH extracts bufotalin and γ -bufotalin (I) from the skin of *Bufo vulgaris formosus*. (I) with 5% KOH-MeOH at 100° affords *Me* γ -isobufotalinate, $\text{C}_{25}\text{H}_{36}\text{O}_5$, m.p. 190—191° (+1EtOH, m.p. 124—125°), which on further treatment with 5% KOH-EtOH at 100° gives *Me* γ -bufotalinate (II), m.p. 215°, which has aldehydic properties. With warm 2.5N-NaOH (II) gives γ -isobufotalinic acid, m.p. 205°, isomeric with (I). The Ac derivative of (I) with O_3 in CHCl_3 below 0° affords CH_2O , $\text{CHO}\cdot\text{CO}_2\text{H}$, $\text{H}_2\text{C}_2\text{O}_4$, and diacetyltio- γ -bufotalinic acid, m.p. 225°. Anhydro- γ -bufotalin with Pd-H_2 in AcOH gives hexahydro- γ -bufotalin and an isomeride, m.p. 212—213°, of dihydroxycholanolic acid. With CrO_3 in AcOH at 0° (I) affords a substance, $\text{C}_{24}\text{H}_{30}\text{O}_5$ or $\text{C}_{24}\text{H}_{32}\text{O}_5$, m.p. 252°. A structure is suggested for (I). J. L. D.

Soya-bean saponin. IV. K. TSUDA and S. KITAGAWA (Ber., 1938, 71, [B], 1604—1609; cf. A., 1938, II, 239).—Soyasapogenol B (I) is very slowly

oxidised by KMnO_4 in boiling COMe_2 to the compound, $\text{C}_{30}\text{H}_{48}\text{O}_3$, decomp. 218° (monoxime, decomp. 244° ; diacetate, m.p. 146.5°). Methylhederagenin (II) (as typical triterpene alcohol) is converted by Cu-bronze at about 270° into CH_2O and methylhedragone, m.p. 203° , $[\alpha]_D^{25} + 104.9^\circ$ in CHCl_3 , identical with the product of the oxidation of (II) with CrO_3 in AcOH . Analogously (I) and Cu-bronze at 270° yield CH_2O and the diketone, m.p. $253\text{--}255^\circ$, $[\alpha]_D^{25} + 57.14^\circ$ in CHCl_3 (dioxime, decomp. 266°), identical with that derived (*loc. cit.*) from (I) and CrO_3 . Dihydrosoyasapogenol C and soyasapogenol C and D with Cu-bronze give CH_2O and the respective monoketones, $\text{C}_{29}\text{H}_{48}\text{O}$, m.p. 207° (monoxime, decomp. $213\text{--}215^\circ$), $\text{C}_{29}\text{H}_{46}\text{O}$, m.p. 215° , $[\alpha]_D^{25} + 84.4^\circ$ in CHCl_3 (monoxime, decomp. 231°), and $\text{C}_{29}\text{H}_{46}\text{O}_2$, m.p. 202° (monoxime, m.p. 223°). Betulin and dihydrobetulin (III) are unchanged when heated with Cu-bronze at $300^\circ/4$ mm. and $250\text{--}300^\circ/3$ mm., respectively. At 330° (III) affords the keto-aldehyde, $\text{C}_{30}\text{H}_{48}\text{O}_2$, decomp. $183\text{--}185^\circ$, $[\alpha]_D^{25} + 11.45^\circ$ in CHCl_3 (dioxime, decomp. 275°), corresponding with dihydrobetulonic acid. The action of Cu on triterpene alcohols, therefore, is a very simple means of preparing triterpene-ketones or -aldehydes and also affords a method for determining the position of their OH groups. H. W.

Condensation of furfuryl bromide with sodium phenoxide. R. PAUL and H. NORMANT (Bull. Soc. chim., 1938, [v], 5, 1148—1153).—Mainly an account of work already abstracted (A., 1937, II, 385). o-Furfurylphenol is converted by Me_2SO_4 and alkali into o-furfurylanisole, b.p. $136^\circ/11$ mm., reduced (H_2 at $110^\circ/60$ atm.—Raney Ni) to o-tetrahydrofurfurylanisole, b.p. $143\text{--}144^\circ/11$ mm. H. W.

4-Benzoyl-2-phenylfuran. R. C. FUSON, C. L. FLEMING, and R. JOHNSON (J. Amer. Chem. Soc., 1938, 60, 1994—1997).— $\text{CHBz}:\text{CMeBz}$ (modified prep.) reduces 0.5 mol. of SeO_2 in dioxan, giving 63% of 4-benzoyl-2-phenylfuran (I), m.p. $113.7\text{--}114^\circ$, which, unlike most furan derivatives, is stable to short treatment with acids, but is degraded by hot 10% NaOH to $(\text{CH}_2\text{Bz})_2$. With $\text{NH}_3\text{--H}_2\text{O--EtOH}$ at $130\text{--}140^\circ$ (I) gives 4-benzoyl-2-phenylpyrrole, m.p. $213.7\text{--}215.5^\circ$ [oxime, m.p. $188.5\text{--}191.5^\circ$ (sinters at 171°)], and with boiling NH_2Ph gives the anil, m.p. $230.5\text{--}231^\circ$, hydrolysed to 4-benzoyl-1:2-diphenylpyrrole, m.p. $240\text{--}241^\circ$ (oxime, m.p. $215.5\text{--}218.5^\circ$). Dypnone and SeO_2 give 2:4-diphenylfuran, but $(\text{CMeBz})_2$ and $\text{CHBz}:\text{CHMe}$ do not react. Ni-hydrogenation of (I) gives 2-phenyl-4- α -hydroxybenzylfuran, m.p. $128.1\text{--}129.1^\circ$ (benzoate, m.p. $123.1\text{--}124.1^\circ$; p-nitrobenzoate, m.p. $109.5\text{--}109.8^\circ$). The oxime, m.p. $149\text{--}149.4^\circ$, of (I) and PCl_5 in Et_2O give 2-phenyl-4-furoanilide, m.p. $192\text{--}193^\circ$, hydrolysed to NH_2Ph and 2-phenyl-4-furoic acid, m.p. $208\text{--}209^\circ$, decarboxylated with difficulty (heating alone at 275°) to 2-phenylfuran. R. S. C.

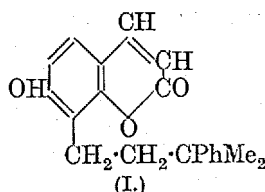
Heterocyclic compounds. VII. Coumarins from resacetophenone and cyclic β -ketonic esters. VIII. Coumarins from alkylcyclohexanone-2-carboxylates and trans- β -decalone-3-carboxylate. N. A. CHOWDHRY and R. D. DESAI (Proc. Indian Acad. Sci., 1938, 8, A, 1—5, 12—19; cf. A., 1938, II, 198).—VII. Et cyclohexanone-2-carboxylate,

resacetophenone, and POCl_3 in boiling C_6H_6 give 7-hydroxy-6-acetyl- Δ^1 -cyclohexeno-1':2'-4:3-coumarin [7-hydroxy-6-acetyl-3:4-tetramethylenecoumarin], m.p. 237° (7-Ac derivative, m.p. 199°), the structure of which is proved by its giving a reddish-violet colour with $\text{FeCl}_3\text{--EtOH}$ and by reduction by Hg--Zn dust and HCl to 7-hydroxy-6-ethyl-3:4-tetramethylenecoumarin. Et 4- (I) and 5-methylcyclohexan-1-one-2-carboxylate (II) give similarly 7-hydroxy-6-acetyl-4', m.p. 262° , and -5'-methyl- Δ^1 -cyclohexeno-1':2'-4:3-coumarin, m.p. 258° , respectively, reduced to 7-hydroxy-4', m.p. 252° (7-Ac derivative, m.p. 146° ; Me ether, m.p. 158°), and -5'-methyl-6-ethyl- Δ^1 -cyclohexeno-1':2'-4:3-coumarin, m.p. 202° (7-Ac derivative, m.p. 167° ; Me ether, m.p. 127°), respectively, which are also obtained directly from (I) or (II), 4-ethylresorcinol, and H_2SO_4 at room temp. Et trans-2-ketodecahydronaphthalene-3-carboxylate (III), m.p. 46° , b.p. $145\text{--}150^\circ/6$ mm. (modified prep. from trans-2-ketodecahydronaphthalene and $\text{Et}_2\text{C}_2\text{O}_4$), the structure of which is proved by KMnO_4 -oxidation to trans-cyclohexane-1:2-diacetic acid, with resacetophenone and POCl_3 in boiling C_6H_6 gives 7-hydroxy-6-acetyl- Δ^2 -trans-octahydronaphtha-2':3'-4:3-coumarin, m.p. 250° , reduced to the 6-Et compound, m.p. 308° (7-Ac derivative, m.p. 172°), which is obtained directly from the ester by 4-ethylresorcinol and H_2SO_4 .

VIII. Condensation of (I), (II), or (III) with phloroglucinol, orcinol, or pyrogallol to give coumarin derivatives is best effected by POCl_3 , but for $m\text{-C}_6\text{H}_4(\text{OH})_2$ and $\alpha\text{-C}_{10}\text{H}_7\text{OH}$ H_2SO_4 is better. For Et 6-methylcyclohexan-1-one-2-carboxylate (IV), however, POCl_3 is more effective in all cases. Colour reactions indicate that the products from orcinol are 5-hydroxy-7-methyl- rather than 7-hydroxy-5-methylcoumarins as assumed by Sen *et al.* (A., 1928, 1254). Fries rearrangement of the tri- and tetra-cyclic acetylcoumarins gives 8-acetylcoumarins, the structure of which is proved by independent synthesis (unpublished) of the 6-acetylcoumarins. The following are prepared by the above methods. 7-Hydroxy-, m.p. 217° (Ac derivative, m.p. 176° ; Me ether, m.p. 123°), 7:8-, m.p. 256° (Ac₂ derivative; m.p. 179° ; Me₂ ether, m.p. 154°), and 5:7-dihydroxy-4'-methyl- Δ^1 -cyclohexeno-1':2'-4:3-coumarin, m.p. 265° (Ac₂ derivative, m.p. 128° ; Me₂ ether, m.p. 133°). 7-Hydroxy-, m.p. 202° (Ac derivative, m.p. 136° ; Me ether, m.p. 118°), 7:8-, m.p. 231° (Ac₂ derivative, m.p. 214° ; Me₂ ether, m.p. 123°), and 5:7-dihydroxy-5'-methyl- Δ^1 -cyclohexeno-1':2'-4:3-coumarin, m.p. 262° (Ac₂ derivative, m.p. 117°). 7-Hydroxy-, m.p. 205° (Ac derivative, m.p. 174° ; Me ether, m.p. 112°), 7:8-, m.p. 227° (Ac₂ derivative, m.p. 140°), and 5:7-dihydroxy-6'-methyl- Δ^1 -cyclohexeno-1':2'-4:3-coumarin, m.p. 275° (Ac₂ derivative, m.p. 127°). 7-Hydroxy-8-acetyl-4', m.p. 135° (semicarbazone, m.p. 236°), and -5'-methyl- Δ^1 -cyclohexeno-1':2'-4:3-coumarin, m.p. 142° (semicarbazone, m.p. 232°). 5-Hydroxy-7:4'-, m.p. 250° (Ac derivative, m.p. 185° ; Me ether, m.p. 140°), -7:5'-, m.p. 260° [called by Sen *et al.* (*loc. cit.*) 7-hydroxy-5:4-dimethyl- and given m.p. 249°] (Ac derivative, m.p. 134° ; Me ether, m.p. 98°), and -7:6'-dimethyl- Δ^1 -cyclohexeno-1':2'-4:3-coumarin, m.p. 235° (Ac derivative, m.p. 124°). 4', m.p. 198° , 5', m.p. 173° , and 6'-Methyl- Δ^1 -cyclo-

hexeno-1': 2'-4: 3- α -naphtha-1: 2-pyrone, m.p. 112°. 7-Hydroxy-, m.p. 245° (Ac derivative, m.p. 192°; Me ether, m.p. 178°), 7: 8-, m.p. 267° (Ac₂ derivative, m.p. 200°), and 5: 7-dihydroxy- Δ^2 -trans-octahydronaphtha-2': 3'-4: 3-coumarin, m.p. 265° (Ac₂ derivative, m.p. 173°); 7-hydroxy-8-acetyl- Δ^2 -trans-octahydronaphtha-2': 3'-4: 3-coumarin, m.p. 167° (semicarbazone, m.p. 258°); Δ^2 -trans-octahydronaphtha-2': 3'-4: 3- α -naphtha-1: 2-pyrone, m.p. 222°; and 5-hydroxy-7-methyl- Δ^2 -trans-octahydronaphtha-2': 3'-4: 3-coumarin, m.p. 313° (Ac derivative, m.p. 184°). 4-Ethylresorcinol and (IV) give 7-hydroxy-6'-methyl-6-ethyl- Δ^1 -cyclohexeno-1': 2'-4: 3-coumarin, m.p. 232° (Ac derivative; Me ether, m.p. 109°). R. S. C.

Natural coumarins. XXXVIII. Action of aluminium bromide and benzene on osthol. E. SPÄTH and P. KAINRATH (Ber., 1938, 71, [B], 1662—1666).—Demethylation is accompanied by addition of C₆H₆ to the side-chain. Osthol is transformed by



AlBr₃ in boiling C₆H₆ into phenyldihydro-osthenol (I), m.p. 171—172° (vac.), converted by an excess of CH₃N₂ in Et₂O or by KOH-Me₂SO₄ into the Me ether, m.p. 133—134°. (I) is hydrogenated (Pd sponge in AcOH at 16°) to phenyltetrahydro-osthenol, m.p. 126—127° (vac.), oxidised (HNO₃) to (CH₂·CO₂H)₂. Oxidation of (I) in alkaline solution by H₂O₂ yields γ -phenyl- γ -methylvaleric acid (p-xenylamide, m.p. 97—98°; anilide, m.p. 115—117°); the acid is obtained synthetically by the action of AlBr₃ and abs. C₆H₆ on γ -isohexolactone. isoButyrophenone is treated with CH₂Br·CO₂Et and Zn filings and the product is boiled with 85% HCO₂H and then with KOH-MeOH, thereby giving a β -phenyl- γ -methylpentenoic acid, b.p. 120—130° (bath)/1 mm., hydrogenated (Pd sponge in AcOH) to β -phenyl- γ -methylvaleric acid (p-xenylamide, m.p. 101—103°). CH₂(CO₂Et)₂ is condensed with NaOEt and CH₂Ph·CHMe·CH₂Br in EtOH and the product is hydrolysed, acidified, and decarboxylated to δ -phenyl- γ -methylvaleric acid (anilide, m.p. 74—76°). H. W.

Natural coumarins. XXXIX. Constitution of umbelliprenin. E. SPÄTH and F. VIERHAPPER (Ber., 1938, 71, [B], 1667—1672).—Angelica seeds are extracted with Et₂O, the solution is evaporated, and the residue is treated with light petroleum of low b.p. The residue obtained from this solvent is subjected to a double lactone separation, whereby lactone closure is effected in each case with AcOH. The lactone fraction (about 0.25% of the drug) contains imperatorin with small amounts of alloimperatorin formed during the distillation, bergapten, and umbelliprenin (I) (= coumarin with the side-chain Me·[CMe·CH·CH₂·CH₂]₂·CMe·CH·CH₂·O· at 6) m.p. 61—63°. It is converted by cold AcOH-H₂SO₄ into umbelliferone (identified also as its Me ether) and an intensely odoriferous, non-phenolic material (II) which is shown by micro-hydrogenation to be heterogeneous. (I) absorbs 4 H₂, showing the presence of three double linkings in the side-chain and one in the coumarin ring. Farnesol is conveniently identified as di-2-

naphthylfarnesylurethane, m.p. 70—71°, which could not be obtained from (II). CMe₂·CH·CH₂Br and Na umbelliferone afford umbelliferone γ -methyl- Δ^8 -butenyl ether, m.p. 70—71°, in small yield. Attempts to obtain the farnesyl ether similarly did not give a cryst. product. H. W.

Structure of β - and γ -tocopherols. O. H. EMERSON (J. Amer. Chem. Soc., 1938, 60, 1741—1742).—Californian wheat-germ oil contains twice as much α - as β -tocopherol (I). CrO₃-oxidation of (I) and γ -tocopherol (II) gives Fernholz's acid (benzylthiuronium salt, m.p. 116—117°) (A., 1938, II, 186). At 360° in CO₂ (II) gives 2: 3: 5: 1: 2-C₆HMe₃(OH)₂. The tocopherols are thus closely related. R. S. C.

5-Chloro-2-hydroxy-3: 6-dimethylthionaphthen.—See B., 1938, 1021.

Synthesis of the ephedrine of the pyrrolidine series. Q. MINGOIA (Congr. int. Quim. pura apl., 1934, 9, V, 174—180; Chem. Zentr., 1936, ii, 3908).—Mg pyrrol bromide and EtCOCl in H₂ yield 2-propionylpyrrole (I), m.p. 52°, and, after refluxing the reaction product, 3-propionylpyrrole, m.p. 110—111°. Bromination of (I) affords 2-(α -bromopropionyl)pyrrole (II), m.p. 131—133°; 2-(α -chloropropionyl)pyrrole (III), m.p. 90—92°, is obtained directly from CHClMe·COCl. With NH₂Me (II) or (III) gives 2-(α -methylamino-propionyl)pyrrole, m.p. 155—156° (picrate, m.p. 180—181°; hydrochloride), which when saturated with H₂ in AcOH in presence of PtO₂ yields the ephedrine of the pyrrolidine series (picrate, m.p. 145—147°; hydrochloride). A. H. C.

Synthesis of indole. K. POLYAKOVA (Maslob. Shir. Delo, 1935, 11, 452).—o-C₆H₄Me·NO₂ and Et₂C₂O₄ give o-nitrophenylpyruvic acid, which is reduced to indole-2-carboxylic acid. The last decomposes to indole and CO₂. CH. ABS. (c)

Alkylene derivatives of cyclic bases. I. Derivatives of 2-aminopyridine. T. M. SHARP (J.C.S., 1938, 1191—1193).—2-Aminopyridine, NaNH₂, and PhMe with the appropriate alkylene dibromide give the following compounds: $\alpha\beta$ -bis-2-pyridylaminoethane, m.p. 134—135° (dihydrochloride, m.p. 239—241°), $\alpha\epsilon$ -bis-2-pyridylamino-n-pentane, m.p. 150° (dihydrochloride, m.p. 164°), $\alpha\zeta$ -bis-2-pyridylamino-hexane, m.p. 152—154° (dihydrochloride, m.p. 216—218°), $\alpha\eta$ -bis-2-pyridylamino-n-heptane, m.p. 104—105° (dihydrochloride, m.p. 203—205°), $\alpha\theta$ -bis-2-pyridylamino-n-octane, m.p. 110—112° (dihydrochloride, m.p. 197—198°), $\alpha\iota$ -bis-2-pyridylamino-n-nonane, m.p. 140—141° (dihydrochloride, m.p. 136—139°), and $\alpha\kappa$ -bis-2-pyridylamino-n-decane, m.p. 122—124° (dihydrochloride, m.p. 149—152°). These compounds have a low toxicity, but are inactive in mouse trypanosomiasis. The expected compounds have not been obtained from CH₂I₂, Br·[CH₂]₃·Br, and Br·[CH₂]₄·Br. F. R. S.

Synthesis of xanthurenic acid and chromatographic experiments. L. MUSAJO (Ric. sci. Progr. tecn., 1936, [ii], 7, II, 95—96; Chem. Zentr., 1936, ii, 3540; cf. A., 1935, 1007, 1268).—Fusion of 4-hydroxy-2-carboxy-, 2-carbethoxy-, or, better, -2-methyl-quinoline with KOH yields an acid identical with xanthurenic acid (probably 3: 4-dihydroxyquinoline-2-

carboxylic acid). Chromatographic analysis on Al_2O_3 of a PhMe extract of urine of rats or rabbits fed on fibrin yields indirubin and a little indigo.

A. H. C.

Quinoline derivatives of 2-amino-*p*-cymene. J. N. LE CONTE (J. Elisha Mitchell Sci. Soc., 1935, 51, 249—250).—8-Methyl-5-isopropylquinoline, b.p. 230—232°/190 mm., prepared from amino- (I) and nitro-cymene (Cohn and Gustavson's method), is reduced (Na-EtOH) to 8-methyl-5-isopropyl-1:2:3:4-tetrahydroquinoline, b.p. 165—167°/27 mm. (I) gave with paraldehyde 2:8-dimethyl-5-isopropylquinoline, m.p. 78°, b.p. 179°/35 mm., 170°/25 mm., reduced to 2:8-dimethyl-5-isopropyl-1:2:3:4-tetrahydroquinoline, m.p. 65°, with CH_2Ac_2 , 2:4:8-trimethyl-5-isopropylquinoline, b.p. 177—178°/22 mm., and with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, 2-hydroxy-4:8-dimethyl-5-isopropylquinoline, m.p. 228—230° (in the last two cases after dehydrating the intermediate cymidides with H_2SO_4). 8-Substituted quinolines do not form methiodides; a *cymylisatin*, m.p. 174°, and 2-chloro-4:8-dimethyl-5-isopropylquinoline, m.p. 197°, are described.

CH. ABS. (c)

Catalytic condensation of acetylene with arylamines. XVII. Simultaneous condensation of arylamines with benzaldehyde and acetylene in presence of HgCl_2 . XVIII. Condensation of acetylene with α - and β -naphthylamine in presence of HgCl_2 . XIX. Condensation of acetylene with *o*-, *m*-, and *p*-toluidine in presence of CuBr. N. KOZLOV (J. Gen. Chem. Russ., 1938, 8, 413—418, 419—423, 475—476).—XVII. CHPh.NPh in EtOH, paraldehyde, and conc. HCl (5 hr. at 100°) yield 2-phenylquinoline, also obtained by saturating a mixture of PhCHO, NH_2Ph , and HgCl_2 with C_2H_2 , at room temp.

XVIII. α - or β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ in EtOH and C_2H_2 in presence of HgCl_2 yield 2-methyl-7:8- or -5:6-benzquinoline; in COMe_2 the product is 2:4-dimethyl-7:8- or -5:6-benzquinoline.

XIX. Condensation of toluidines with C_2H_2 is catalysed by CuBr as well as by CuCl. R. T.

Octahydropyridocoline-norlupinane relationship. II. G. R. CLEMO, J. G. COOK, and R. RAPER (J.C.S., 1938, 1183—1185).—Et hexahydroanthranilate and $\text{Cl}[\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$ give *Et* β -*o*-carbethoxy-hexahydroanilinopropionate, b.p. 135—140°/1 mm., cyclised (K) to 4-ketodecahydroquinoline, b.p. 135—140°/15 mm. [*picrate*, m.p. 175°; *picrolonate*, m.p. 201° (decomp.); *Bz* derivative, m.p. 145°]. Reduction of the ketone by either the Wolff or the Clemmensen method affords *trans*-decahydroquinoline [*picrolonate*, m.p. 202° (decomp.)]; the Clemmensen method also gives an isomeric base (*picrate*, m.p. 169°). The *cis*-form of decahydroquinoline is converted by boiling HCl into the *trans*-form. Hence this cannot be used to test the hypothesis put forward (cf. A., 1936, 1526). *Et* 4-methylpiperidine-2-carboxylate, b.p. 70°/1 mm. (*picrate*, m.p. 142°), prepared from the acid, and γ -bromobutyronitrile give γ -2-carbethoxy-4-methylpiperidinobutyronitrile, b.p. 135°/1 mm., which is hydrolysed to *Et* γ -2-carbethoxy-4-methylpiperidinobutyrate, b.p. 136—138°/1 mm., cyclised to 1-keto-8-methyloctahydropyridocoline, b.p. 115—120°/15 mm.

[*picrate*, m.p. 178° (decomp.)]. Reduction of the ketone by the Wolff method yields 8-methyloctahydropyridocoline A, b.p. 47—48°/1 mm. (*picrate*, m.p. 150°; *picrolonate*, m.p. 197°, and a small quantity of a second form; *methiodide*, m.p. 212°). Clemmensen reduction gives a base B, b.p. 47—48°/1 mm. (*picrate*, m.p. 189°, and a second form, m.p. 152°; *picrolonate*, m.p. 138°; *methiodide*, m.p. 181°). The bases are not interconvertible.

F. R. S.

The 4-aminoacridine-1-carboxylic acid of Matsumura. K. LEHMSTEDT (Ber., 1938, 71, [B], 1609—1610).—The nitroacridonecarboxylic acid obtained by Matsumura (A., 1938, II, 246) from 5-nitrodiphenylamine-2:2'-dicarboxylic acid is 3-nitroacridone-5-carboxylic acid since when decarboxylated and then treated with NPhMe_2 it gives 3-nitro-9-*p*-dimethylaminophenylacridine. The compounds obtained by Matsumura should therefore be re-numbered (his positions are placed in parentheses): 3(1)-nitroacridone-5(4)-carboxyl chloride, decomp. 299°; 3(1)-aminoacridone-5(4)-carboxylic acid, m.p. 289—290°; 3(1)-aminoacridine-5(4)-carboxylic acid, decomp. 273—274° (hydrochloride, decomp. 245—250°).

H. W.

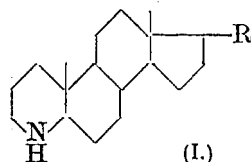
Complex salts of α -methyl-*o*-phenanthroline. P. PFEIFFER and W. CHRISTELEIT (J. pr. Chem., 1938, [ii], 151, 127—133).—The introduction of 2-Me into the phenanthroline mol. has no marked influence on the ability of the two N to unite with metallic atoms. The colours of the salts may differ considerably from those of the simpler base. α -Methylphenanthroline gives a *perchlorate*, m.p. 205—208° (decomp.), a *picrate*, and a *platinichloride* (+4 H_2O), which slowly becomes discoloured at 180°. The following complex salts are described:

$[\text{Fe}(\text{C}_{13}\text{H}_{10}\text{N}_2)_3](\text{ClO}_4)_2$, which does not appear to exist in isomeric forms; $[\text{Fe}(\text{C}_{13}\text{H}_{10}\text{N}_2)_3]\text{SO}_4\cdot 12\text{H}_2\text{O}$; $[\text{Ni}(\text{C}_{13}\text{H}_{10}\text{N}_2)_3](\text{ClO}_4)_2$; $[\text{Cu}(\text{C}_{13}\text{H}_{10}\text{N}_2)_2\text{Cl}_2]$; $[\text{Cu}(\text{C}_{13}\text{H}_{10}\text{N}_2)_2](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$; $[\text{Ag}(\text{C}_{13}\text{H}_{10}\text{N}_2)_2]\text{NO}_3$.

H. W.

Sterol derivatives containing nitrogen in the nucleus. C. C. BOLT (Rec. trav. chim., 1938, 57, 905—910).—Cholestenone with O_3 in AcOH, followed by H_2O , yields a CO-acid the oxime of which is reduced (Na-EtOH) to the corresponding NH_2 -acid, isolated (by acidification with AcOH and extraction with Et_2O) as its lactam, m.p. 253—255°, $[\alpha]_D^{18} +44^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (*Ac* derivative, m.p. 136—137°). Reduction (Na- $\text{C}_5\text{H}_{11}\cdot\text{OH}$) of the lactam yields the amine [(I), $\text{R} = \text{C}_8\text{H}_{17}$], m.p. 116—117°, $[\alpha]_D +48^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (*Ac* derivative, m.p. 132—132.5°). Similarly testosterone acetate yields (with elimination of the *Ac* group) a keto-acid, $\text{C}_{18}\text{H}_{28}\text{O}_4$, m.p. 206.5—207° (*oxime*, m.p. 199—202°), lactam, m.p. 262—263°, $[\alpha]_D^{18} +33^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (*Ac* derivative, m.p. 164—167°), and amine [(I), $\text{R} = \text{OH}$], m.p. 202—203°, $[\alpha]_D^{18} +0.28^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (*Ac* derivative, m.p. 180.5—181.5°). M.p. are corr.

A. LI.



Hydantoins derived from the analogues of methyl $\beta\beta'$ -dichloroisopropoxyethyl ketone. B. B. ALLEN [with H. R. HENZE] (J. Amer. Chem.

Soc., 1938, **60**, 1796—1797).—*Ph* α - β ' β '-dichloroisopropoxyethyl ketone [prep. from $(\text{CH}_2\text{Cl})_2\text{CH}\cdot\text{O}\cdot\text{CHMe}\cdot\text{CN}$ and MgPhBr], b.p. $169^\circ/4$ mm., or the corresponding alkyl ketones with KCN (1.25 mol.) and $(\text{NH}_4)_2\text{CO}_3$ (3 mols.) at 55 — 62° give 5-phenyl-5- α - β ' β '-dichloroisopropoxyethylhydantoin, m.p. 187 — 188° , 5-methyl-, m.p. 229 — 230° , and 5-ethyl-5- α - β ' β '-dichloroisopropoxyethylhydantoin, m.p. 198.5 — 199.5° , 5- α - β ' β '-dichloroisopropoxyethyl-5-n-propyl-, m.p. 211.5 — 212.5° , -isopropyl-, m.p. 146.5 — 147.5° , -n-butyl-, m.p. 206.5 — 207.5° , -sec-butyl-, m.p. 149.5 — 151° , -n-amyl-, m.p. 181 — 182° , and -isoamyl-hydantoin, m.p. 187 — 187.5° . M.p. are corr.

R. S. C.

Bromo-ethers derived from hydantoin having terminal ethylenic linkings in the 5 position. (MISSIS) D. A. HAHN, M. J. McLEAN, and H. T. MURPHY (J. Amer. Chem. Soc., 1938, **60**, 1927—1929).—Both forms of Et 5-benzylidene-3-methylhydantoin-1-acetate (Litzinger, A., 1934, 534) with Br give not only the compound (I), $\text{C}_{17}\text{H}_{21}\text{O}_5\text{N}_2\text{Br}$, m.p. 113 — 113.5° , but also an isomeride (II), m.p. 92 — 94° , thereof. (I) and (II) are shown by their absorption spectra to be saturated hydantoin and are forms of Et 5-ethoxy-5- α -bromobenzyl-3-methylhydantoin-1-acetate. 5-Benzylidene-1:3-dimethylhydantoin gives similarly forms, m.p. 141 — 143° and 119.5 — 121.5° , respectively, of 5-ethoxy-5- α -bromobenzyl-1:3-dimethylhydantoin, which have similar absorption spectra.

R. S. C.

Pyrazoline local anæsthetics. I. Derivatives of benzylidene- and anisylidene-acetone. H. B. NISBET (J.C.S., 1938, 1237—1241).—Benzylidene-acetone, NHMe_2 , HCl , and CH_2O give 1-dimethylamino-5-phenyl- Δ^4 -penten-3-one hydrochloride, m.p. 157° , the phenylhydrazone, m.p. 169° , of which is isomerised (AcOH) to 1:5-diphenyl-3- β -dimethylaminoethylpyrazoline hydrochloride, m.p. 176° , and the *p*-tolylhydrazone to the 5-phenyl-1-*p*-tolyl compound, m.p. 177 — 178° . The following compounds have been similarly prepared: 1:5-diphenyl-3- β -piperidinoethylpyrazoline hydrochloride, m.p. 197° ; *p*-tolylhydrazone, m.p. 199° , of 1-piperidino-5-phenyl- Δ^4 -penten-3-one hydrochloride; 5-phenyl-1-*p*-tolyl-, m.p. 212° , and -1-*p*-ethoxyphenyl-3- β -piperidinoethylpyrazoline hydrochloride, m.p. 192 — 193° ; 1-dimethylamino-5-*p*-anisyl- Δ^4 -penten-3-one hydrochloride, m.p. 155° (*p*-tolylhydrazone, m.p. 170° ; 1-phenyl-, m.p. 173° , and 1-*p*-tolyl-5-*p*-anisyl-3- β -dimethylaminoethylpyrazoline hydrochloride, m.p. 184° ; 1-diethylamino-5-*p*-anisyl- Δ^4 -penten-3-one hydrochloride, m.p. 146° (phenylhydrazone, m.p. 171°); 1-phenyl-5-*p*-anisyl-3- β -diethylaminoethylpyrazoline, m.p. 27° (tartrate, m.p. 80°); 1-di-n-propylamino-5-*p*-anisyl- Δ^4 -penten-3-one hydrochloride, m.p. 150° (phenylhydrazone, m.p. 180°); 1-phenyl-5-*p*-anisyl-3- β -di-n-butylaminoethylpyrazoline, m.p. 66 — 68° (phenylhydrazone, m.p. 167 — 168°); 1-phenyl-5-*p*-anisyl-3- β -di-n-butylaminoethylpyrazoline, m.p. 26 — 27° ; 1-piperidino-5-*p*-anisyl- Δ^4 -penten-3-one hydrochloride phenylhydrazone, m.p. 188° ; 1-phenyl-5-*p*-anisyl-3- β -piperidinoethylpyrazoline, m.p. 88° [hydrochloride, m.p. 215° , acid sulphate, m.p. 172° (decomp.), and tartrate, m.p.

115° (decomp.)]; *p*-tolylhydrazone, m.p. 176 — 177° , of 1-piperidino-5-*p*-anisyl- Δ^4 -penten-3-one hydrochloride; 1-*p*-tolyl-5-*p*-anisyl-3- β -piperidinoethylpyrazoline hydrochloride, m.p. 204° ; 1-dibenzylamino-5-*p*-anisyl- Δ^4 -penten-3-one hydrochloride, m.p. 225 — 230° (decomp.) (phenylhydrazone, m.p. 235 — 240°); and 1-phenyl-5-*p*-anisyl-3-*p*-dibenzylaminoethylpyrazoline (?), b.p. 300 — $301^\circ/1$ mm. 1-Piperidino-5-*p*-anisyl- Δ^4 -penten-3-one hydrochloride with $\text{NHPh}\cdot\text{NH}_2$ does not give a hydrazone but a ketazine (succinate, m.p. 137°); it forms an oxime, m.p. 166° (hydrochloride, m.p. 208°). Increase in size, up to NPr_2 , of the NAlk_2 group increases the local anæsthetic potency and to a smaller degree the toxicity.

F. R. S.

Preparation of 2:6-dialkoxy-4-methyl-5-ethylpyrimidines. Y. F. CHI and D. CHIN (J. Chem. Eng. China, 1938, **5**, 19—20).—4-Methyl-5-ethyluracil is transformed by $\text{POCl}_3\text{--PCl}_5$ at 120° into 2:6-dichloro-4-methyl-5-ethylpyrimidine, b.p. 130 — $131^\circ/6$ mm., m.p. 25 — 27° . This is converted by the requisite Na alkoxide in the appropriate alcohol at room temp. into 2:6-dimethoxy-, b.p. $118^\circ/7$ mm., and 2:6-diethoxy-, b.p. 138 — $139^\circ/17$ mm., -4-methyl-5-ethylpyrimidine.

H. W.

Pyrimidines: molecular rearrangement of 2:6-dimethoxy-4-methyl-5-n-butylpyrimidine. Y. F. CHI, C. WEI, and N. S. PAN (J. Amer. Chem. Soc., 1938, **60**, 1719—1721).—2:6-Dichloro-4-methyl-5-n-butylpyrimidine [prep. from 4-methyl-5-n-butyluracil (I) by $\text{POCl}_3\text{--PCl}_5$ at 120°], b.p. $171^\circ/23$ mm., with NaOR in ROH gives 2:6-dimethoxy- (II), b.p. $159^\circ/29$ mm., -diethoxy-, b.p. $174^\circ/27$ mm., -di-n-propoxy-, b.p. 193 — $194^\circ/23$ mm., -di-n-butoxy-, b.p. $219^\circ/29$ mm., and -diallyloxy-4-methyl-5-n-butylpyrimidine, b.p. 192 — $193^\circ/31$ mm. At 250 — 270° (II) gives 1:3:4-trimethyl-5-n-butyluracil (III), m.p. 54 — 55° , also obtained from (I) by $\text{Me}_2\text{SO}_4\text{--NaOH}$. With MeI at 50° or 100° (I) is only partly rearranged, yielding 2-keto-6-methoxy-3:4-dimethyl-5-n-butylpyrimidine (IV), b.p. 183 — $184^\circ/1$ mm., 235 — 236° (decomp.)/31 mm., hydrolysed by hot dil. HCl to 3:4-dimethyl-5-n-butyluracil, m.p. 151 — 152° , and converted at 300 — 360° into (III). When kept in MeI at room temp. for 2 weeks, (I) gives a little (IV), probably formed by way of (III).

R. S. C.

Pyrimidines: synthesis of 4-methyl-5-n-propylcytosine. Y. F. CHI and K. H. CHANG (J. Amer. Chem. Soc., 1938, **60**, 1721—1723).—6-Keto-2-thiol-4-methyl-5-n-propylpyrimidine [prep. from $\text{CHPr}^t\text{Ac}\cdot\text{CO}_2\text{Et}$, $\text{CS}(\text{NH}_2)_2$, and NaOEt], m.p. 209 — 209.5° , RHal , and NaOEt in EtOH at 100° give 6-keto-2-methyl-, m.p. 180 — 181° , -ethyl- (I), m.p. 92 — 93° , and -n-propyl-thiol-4-methyl-5-n-propylpyrimidine, m.p. 89 — 90° , hydrolysed by HBr or HCl to 4-methyl-5-n-propyluracil, m.p. 247 — 248° , which with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ gives Et 6-keto-4-methyl-5-n-propylpyrimidine-2-thiolacetate, m.p. 100 — 101° (corresponding acid, $+\alpha\text{H}_2\text{O}$, m.p. 105 — 106°). With POCl_3 at 120 — 130° (I) gives 6-chloro-2-ethylthiol-4-methyl-5-n-butylpyrimidine, b.p. 165 — $166^\circ/11$ mm., converted by $\text{NH}_3\text{--EtOH}$ at 160 — 170° into the 6- NH_2 -compound, m.p. 86 — 87° , which with conc. HBr yields 4-methyl-5-n-propylcytosine, m.p. 317 —

318° (decomp.) (*hydrobromide*, m.p. 253—254°; *hydrochloride*, m.p. 235°). R. S. C.

Complex salts of the alkali and alkaline-earth metals [with o-phenanthroline and dipyridyl].—See A., 1938, I, 529.

Anthraquinonylguanidines. M. BATTEGAY (Congr. int. Quim. pura apl., 1934, 9, IV, 337—351; Chem. Zentr., 1936, ii, 3299).—1-Amino-4-benzamido-anthraquinone and $\text{CN}\cdot\text{NH}_2\cdot 2\text{HCl}$ in *m*-cresol (cf. A., 1932, 405; 1935, 1254) yield py-C-amino-4-benzamido-1:9-anthrapyrimidine, m.p. 295° (orange solution in H_2SO_4), dyeing cotton salmon-red from an orange-red vat. Treatment with BzCl and $\text{C}_5\text{H}_5\text{N}$ in PhNO_2 for 1 hr. at 180° yields the C-aminobenzoyl derivative and a compound, $\text{C}_{36}\text{H}_{22}\text{O}_4\text{N}_4$, which dyes cotton yellow. Similarly 1:4-diaminoanthraquinone affords py-CC'-diamino-1:9:4:10-anthradipyrimidine (I), m.p. <300°. (I) gives a yellow-red fluorescent solution in H_2SO_4 and a nitrate, $\text{C}_{16}\text{H}_{10}\text{N}_6\cdot 2\text{HNO}_3$. 1:5-Diaminoanthraquinone gives py-C-amino-5-guanido- (blue-red in H_2SO_4) and -5-amino-1:9-anthrapyrimidine, m.p. <300°, which dye cotton brown after oxidation. A. H. C.

Indigotin. I. Nitration of indigotin. II. Ozonisation of indigotin. III. Reaction between indigotin, aromatic iodides, and potassium carbonate. J. VAN ALPHEN (Rec. trav. chim., 1938, 57, 837—846, 911—914, 915—920).—I. Indigotin (I) is decomposed by HNO_3 alone, or in conc. H_2SO_4 , 7% oleum, or glacial AcOH , but with HNO_3 in Ac_2O at -10° gives, according to the amount of HNO_3 , 5'-mono-, 5:5'-di-, and 5:7:5'-tri-nitro-2-acetoxydi-indoxyl, converted by heating at 200—250° or by boiling with PhNO_2 into the mono-, di-, and tri-nitro-indigotins, none of which melts below 300°. HNO_3 in $(\text{Pr}^c\text{CO})_2\text{O}$ gives 5:5'-dinitro-2-n-butyroxydi-indoxyl, which loses PrCO_2H at 250°, whilst HNO_3 in AcCl gives 5-chloroisatin. 2:2'-Diaceoxy-2:2'-di-indoxyl with HNO_3 in Ac_2O at -10° yields 5:7:5'-trinitro-2:2'-diaceoxydi-indoxyl, which when boiled with PhNO_2 gives the trinitroindigotin.

II. With 1 mol. of O_3 in dry CHCl_3 , (I) yields an ozonide (decomp. 100—140°) which with H_2O gives isatin; excess of O_3 gives a less stable product which gives no isatin. O_3 in dry EtOAc , followed by H_2O , gives isatin, but in wet EtOAc yields isatinic anhydride.

III. When boiled with PhI , K_2CO_3 , and Cu-bronze in PhNO_2 , (I) gives (in poor yields) o-NHPh-C₆H₄-CO₂H and bis-(1-phenylindoxyl)hydroxyacetic acid (partly decomposed at 320°), which when heated gives acridine, CO_2 , and H_2O , and is oxidised (CrO_3) to bis-1-phenylindoxyl ketone (does not melt at <320°). The p-tolyl-, p-anisyl-, and p-diphenylhydroxy-acids have similar properties. The mechanism of the reaction is discussed. A. LI.

Peganine. XIV. Pyracridone (= α-quinolone). E. SPÄTH and F. KUFFNER (Ber., 1938, 71, [B], 1657—1661).—Pyracridone (I) (Reissert, A., 1895, i, 244; Rāth, A., 1931, 852) and α-quinolone (Seide, A., 1925, i, 159) are shown to be identical with one another and to be hydrogenated (Pd-sponge in AcOH) to the H_4 -base (II) obtained by Späth and

Platzer (A., 1936, 215). They are therefore
$$\text{o-C}_6\text{H}_4\text{<}\begin{matrix} \text{CO}\cdot\text{N}\cdot\text{CH}\cdot\text{CH} \\ \text{N}=\text{C}\cdot\text{CH}\cdot\text{CH} \end{matrix}$$
 Further catalytic dehydrogenation of (II) gives (I), which is also obtained from 2-hydroxypyridine and isatoic anhydride. In the production of (I) from 2-chloropyridine and o-NH₂-C₆H₄-CO₂H the initial step is the formation of o-2-pyridylaminobenzoic acid, which reacts in its tautomeric form $\text{o-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}\begin{matrix} \text{NH}\cdot\text{CH} \\ \text{CH}=\text{CH} \end{matrix}\text{CH}$ to (I). H. W.

Carnosine nitrate, m.p. 227° (decomp.); **anserine nitrate**, m.p. 226° (decomp.).—See A., 1938, III, 739.

Chromic acid oxidation of uric acid. A. LÉVÊQUE and J. MOULIN (Bull. Sci. Pharmacol., 1936, 43, 213—220; Chem. Zentr., 1936, ii, 3146).—A mixture of 1 vol. of 1% $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ and 5 vols. of saturated aq. K_2SO_4 is, unlike ordinary aq. $\text{K}_2\text{Cr}_2\text{O}_7$, stable at the b.p.; it oxidises uric acid to CO_2 and $\text{CO}(\text{NH}_2)_2$, the latter suffering further hydrolysis (84% after 24 hr., 100% in presence of Ag_2SO_4). Titration of excess of $\text{K}_2\text{Cr}_2\text{O}_7$ shows that 1 mol. of uric acid = 6I and the method is therefore preferable to direct oxidation with I (1 mol. = 2I).

A. H. C.

Phthalocyanines and associated compounds. XIV. Metallic derivatives. P. A. BARRETT, D. A. FRYE, and R. P. LINSTAD (J.C.S., 1938, 1157—1163).—Excess of Li amylxide and o-C₆H₄(CN)₂ give Li₂ phthalocyanine, whilst excess of the nitrile affords Li H phthalocyanine; the Li₂ compound is sol. in cold EtOH and may be used for the prep. of other phthalocyanines by double decomp. The following are described: (Pc = C₃₂H₁₆N₈), Ag (PcAg or ? PcHAg), Hg, Sb₂, chloroantimony (PcSbCl), and chloroferric (PcFeCl) phthalocyanines, and Pd chlorophthalocyanine (C₃₂H₁₅N₈ClPd). Fe^{II} phthalocyanine forms hexa-aniline, hexa-o-toluidine, and dipyridine additive compounds. F. R. S.

Quinoline derivatives. V. T. N. GHOSH (J. Indian Chem. Soc., 1938, 15, 240—242; cf. A., 1938, II, 296).— $\text{CHAc}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{CO}_2\text{H}$ and $\text{NHPh}\cdot\text{NH}_2$ in EtOH give H_2S and 3:βδ-triketo-2-phenyl-5-γ-n-amyl-Δ⁴-1:2:4-triazoline, m.p. 105—106° (and an oil, possibly a further condensation product with $\text{NHPh}\cdot\text{NH}_2$), which with NH_2Ph at 160—170° gives β-anilo-3:δ-diketo-2-phenyl-5-γ-n-amyl-Δ⁴-1:2:4-triazoline, m.p. 205—207°, converted by H_2SO_4 at 110° into 3-keto-2-phenyl-5-2':4'-dimethylquinolyl-3'-Δ⁴-1:2:4-triazoline, m.p. 295°. 3:βδ-Triketo-5-γ-n-amyl-Δ⁴-1:2:4-triazoline with N_2H_4 in boiling EtOH gives the azine, m.p. 160°, and with NH_2Ph at 150—180° gives β-anilo-3:δ-diketo-5-γ-n-amyl-Δ⁴-1:2:4-triazoline, m.p. 226—227°, from which no quinoline derivative could, however, be obtained.

R. S. C.

Action of nitric acid on derivatives of coumarono(2':3':3:2)indole. S. R. CAWLEY and S. G. P. PLANT (J.S.C., 1938, 1214—1218).—The p-nitrophenylhydrazones, m.p. 186°, of tetrahydro-γ-pyrone does not undergo the Fischer reaction. Coumaranone and $\text{NHPh}\cdot\text{NH}_2$ give coumarono-(2':3':3:2)indole, m.p. 197°, which forms 1-Ac,

m.p. 156°, 1-Bz, m.p. 177°, and 1-cinnamoyl derivatives, m.p. 108—112°, and *Et coumarono*(2' : 3' : 3 : 2)-indole-1-carboxylate, m.p. 95°. Nitration of these derivatives in AcOH yields respectively 3(or 2)-nitro-2(or 3)-acetoxy-1-acetyl-, m.p. 142°, -1-benzoyl-, m.p. 185°, and -1-cinnamoyl-2 : 3-dihydrocoumarono-(2' : 3' : 3 : 2)indole, m.p. 157—159° [with mononitro-1-cinnamoylcoumarono(2' : 3' : 3 : 2)indole, m.p. 243—247°], and *Et* 3(or 2)-nitro-2(or 3)-acetoxy-2 : 3-dihydrocoumarono(2' : 3' : 3 : 2)indole-1-carboxylate, m.p. 120°. These NO₂-compounds do not give crystal products with alkalis. Coumaranone-p-nitrophenylhydrazones, m.p. 192—194°, is converted (HCl) into 5-nitrocoumarono(2' : 3' : 3 : 2)indole, m.p. 270—275° (1-cinnamoyl derivative, m.p. 220°). Coumaranone-o-, m.p. 179—181°, and -m-nitrophenylhydrazones, m.p. 168—169°, do not form indoles. 3-Acetylcoumarono-(2' : 3' : 1 : 2)-β-naphthindole, m.p. 169°, gives (HNO₃-AcOH) a NO₂-derivative, m.p. 234—236°, and the corresponding 3-Bz compound, m.p. 201°, similarly yields a NO₂-derivative, m.p. 241—242°. F. R. S.

Cyanine dyes.—See B., 1938, 1104.

The new ergot alkaloids. A. STOLL and E. BURCKHARDT (Schweiz. med. Woch., 1936, 66, 353—354; Chem. Zentr., 1936, ii, 3106; cf. A., 1935, 1256).—Following Kharasch *et al.* (A., 1936, 489), comparison of the m.p. and [α] of ergometrine, ergobasine, ergotocine, and their hydrochlorides shows them to be identical, small deviations (A., 1935, 1512) being due to resin-solvent impurities. A. H. C.

Synthetic anti-malarials [N-substituted 8-amino-6-methoxyquinolines, and some derivatives of quinine]. R. F. A. ALTMAN (Rec. trav. chim., 1938, 57, 941—963; cf. A., 1935, 1017, and Magidson *et al.*, A., 1934, 82, 417, 1230).—α-Heptane-, -octane-, and -nonane-diols with conc. HCl at 95° in presence of petroleum (b.p. 90—120°) yield ω-chloro-heptan-, b.p. 120°/13.5 mm. (phenylcarbamate, m.p. 76—77°), -octan-, b.p. 139°/18.5 mm. (phenylcarbamate, m.p. 77°; m-nitrophenylcarbamate, m.p. 62°), and -nonan-α-ol, b.p. 146.5°/14 mm. (phenylcarbamate, m.p. 67°; m-nitrophenylcarbamate, m.p. 57°), which when heated in sealed tubes at 120—160° with NH₄Et₂ yield respectively ω-diethylamino-heptan-, b.p. 132°/9.5 mm., -octan-, b.p. 151°/12 mm. (p-nitrobenzoate, m.p. 74°), and -nonan-α-ol, b.p. 161.5°/12 mm. (p-nitrophenylcarbonate, m.p. 76—76.5°). These with SOCl₂ in C₆H₆ give the α-chloro-ω-diethylamino-compounds, b.p. 126°/15 mm., 130.5°/11 mm., and 145°/10 mm. respectively, which when heated in sealed tubes at 130—170° with a slight excess of 8-amino-6-methoxyquinoline afford 8-(ω-diethylamino-heptylamino)- (dihydrochloride, m.p. 115°), -octylamino)-, b.p. 206°/0.5 mm. (dihydrochloride, m.p. 112—113°; dihydrobromide, m.p. 84°), and -nonylamino)-6-methoxyquinoline, b.p. 218°/0.5 mm. (dihydrochloride, m.p. 105—106°; oxalate, m.p. 86°). These three compounds are very active against malaria in birds. They attack the gametes.

Treatment of quinine hydrochloride with SOCl₂ in CHCl₃ at 20° yields (unstable) quinine chloride monohydrochloride, decomp. 100°, and at 100° the dihydrochloride, m.p. 183° (decomp.), which when heated at 150° with NHMe₂ gives dimethylamino- [picrolonate,

m.p. 170° (decomp.)], and with NH₄Et₂, diethylamino-quinine [picrolonate, m.p. 155° (decomp.)]. Quitenine with SOCl₂ at 100° gives the acid chloride of quitenine chloride monohydrochloride, m.p. 195—200° (decomp.), which yields with H₂O, quitenine chloride dihydrochloride, m.p. ~205° (decomp.), with MeOH the Me, m.p. 185—186° (decomp.), and with EtOH the Et ester dihydrochloride, m.p. ~206° (decomp.). These quinine derivatives are inactive against malaria. A. Li.

Alkaloids of Chinese gelsemium, Kou Wen. Y. F. CHI, Y. S. KAO, and Y. T. HUANG (J. Amer. Chem. Soc., 1938, 60, 1723—1724).—Mixed roots, stems, and leaves of Kou Wen contain koumine (formula, C₂₀H₂₂ON₂, confirmed), m.p. 168° [unaffected by Ac₂O; hydrochloride, m.p. 258°; hydrobromide, m.p. 268—269°; sulphate, m.p. 261—262°; nitrate, m.p. 249—250°; platinichloride, m.p. >310°; methiodide, anhyd. and +H₂O, m.p. 230° (decomp.)], gelsemine (I), (anhyd.) amorphous and (+COMe₂), m.p. 176—178° (hydrochloride, m.p. 303°; nitrate, m.p. 288°; methiodide, m.p. 284°), and koumidine, C₁₉H₂₅O₄N₂, new m.p. 299°. Chou's kouminine (A., 1932, 101; 1936, 618) was a mixture of (I) and other bases. R. S. C.

Veratrine alkaloids. III. Degradation of cevine. Question of coniine. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1938, 124, 659—666; cf. A., 1937, II, 355, 473).—Distillation of cevine (I) with NaOH-CaO yields β-pipecoline, much product of higher b.p. which could not be investigated, and a fraction, b.p. 160°, now identified as 5-methyl-2-ethylpiperidine (II); the formation of coniine (III) could not be detected. Hydrogenation of 5-methyl-2-ethylpyridine (IV) gives a mixture of stereoisomeric piperidines the 3 : 5-dinitrobenzoyl derivative of which does not depress the m.p. of that of (II). Further (II) is dehydrogenated by Zn dust to (IV), identified as the picrate. Hence (III) is not a product of the distillation of (I) with NaOH-CaO or Zn dust and need not be further considered in the problem of the structure of the alkaloid. The dicyclic base C₁₀H₁₆N obtained from the *tert.* base fraction of the NaOH-CaO distillation yields a picrate which does not depress the m.p. of that of 2-ethyl-octahydropyrococline (Clemo and Metcalfe, A., 1937, II, 467) but the methiodide obtained from the base recovered from the picrate does not melt sharply so that the base appears to be a mixture of stereoisomerides. In the higher-boiling fractions a portion, b.p. 207°/760 mm., gave a picrate, analysis of which indicated the base to be C₁₁H₂₁N; its homogeneity is doubtful. Since the *tert.* base containing O (*loc. cit.*) reacts with MgMeI it appears to contain OH. From the fraction, b.p. 230—240°/760 mm., crystals, (?) C₁₁H₁₉ON, m.p. 153—156° after softening, separated. The slight basic fractions obtained by the distillation of (I) with Zn dust contain β-picoline but chiefly (IV), which gives isocinchomeronic acid when oxidised. A small intermediate fraction appears to be 2 : 5-dimethylpyridine. H. W.

Sophora alkaloids. II. Alkaloids of the seeds of S. tetraptera. L. H. BRIGGS and W. S. TAYLOR (J.C.S., 1938, 1206—1207).—The seeds are shown to

contain mostly matrine, a little methylecystine, and a base [aurichloride, m.p. 186° (decomp.)]. F. R. S.

Strychnos alkaloids. C. Transformations of chlorostyrychnine and its dihydro-compound. H. LEUCHS and K. STEINBORN (Ber., 1938, 71, [B], 1577—1585).—Strychnine dissolved in 12N-HCl at 0° is rapidly converted by Cl₂ in CCl₄ into chlorostyrychnine (I), C₂₁H₂₁O₂N₂Cl, m.p. 235° (vac.) after softening (*perchlorate*), catalytically reduced (PtO₂ in 50% AcOH) to chlorodihydrostrychnine and some *trichlorostyrychnine* (+0.5EtOH), m.p. 139—141° (decomp.) or m.p. (after resolidification, vac.) 206—208°, [α]_D²⁰ —477°/d in CHCl₃ (*hydrochloride*; *hydrobromide*), hydrogenated (PtO₂ in 50% AcOH) to dihydrostrychnine. PhCHO, (I), and NaOEt in boiling EtOH afford *chlorobenzylidenestrychnine*, m.p. 252° (vac.) after softening, [α]_D²⁰ —589°/d in CHCl₃, hydrogenated to *chlorobenzylidihydrostrychnine* (II), m.p. 216°, [α]_D²⁰ —64.4°/d in CHCl₃; this is also obtained by chlorination of benzylidihydrostrychnine and is converted by NaOEt into two or more *iso*-bases which form isomorphous mixtures from which a compound, C₂₈H₂₈O₂N₃Cl, m.p. 246°, [α]_D²⁰ —256°/d in CHCl₃, has been separated. (I) is oxidised by air in presence of Fehling's solution to *chloro-9-hydroxystrychnine* (*ψ -chlorostyrychnine*) (+3H₂O), m.p. 130° (decomp.), or (anhyd.), m.p. 240°, [α]_D¹⁹ —132°/d in CHCl₃ free from EtOH, obtained also by the chlorination of *ψ -strychnine*, reduced by Zn dust and 2.5N-HCl to (I) and transformed by MeOH into *chloro-9-methoxystrychnine*, m.p. (indef.) 168—169° (vac.), [α]_D¹⁹ —117°/d in CHCl₃. Oxidation of (I) by KMnO₄ in COMe₂ at 0—2° gives *chlorostyrychninonic acid*, m.p. 270° (indef.; decomp.), and *chlorodihydrostrychninonic acid*, m.p. 305° (decomp.). Chlorination of dihydrostrychnine yields *chlorodihydrostrychnine* (III), m.p. (air-dried or dried at 100°) 190° (decomp.) or, after long keeping, m.p. 208—210° after softening at 190°; this with PhCHO in KOH-EtOH gives *chlorobenzylidenedihydrostrychnine*, m.p. 275° (vac.), [α]_D²⁰ —225°/d in CHCl₃, hydrogenated (PtO₂ in 50% AcOH) to (II). Restricted treatment of (III) with NaOMe in boiling MeOH leads to *isochlorodihydrostrychnine* I, usually, m.p. 198°, occasionally m.p. 222° after softening at 198°, [α]_D¹⁹ —40.7°/d in CHCl₃ (*hydrochloride*; *hydrobromide*), hydrogenated (PtO₂ in 50% AcOH) to *isodihydrostrychnine*; with PhCHO and NaOEt in boiling EtOH it yields *isochlorobenzylidenedihydrostrychnine*, m.p. 217°, [α]_D¹⁹ —716°/d in CHCl₃ (*hydrochloride*), also obtained similarly from the non-isomerised chlorodihydro-base. More drastic treatment of (III) with NaOEt-EtOH affords *isochlorodihydrostrychnine* II, m.p. about 250° (decomp.) or, after desiccation at 125°/15 mm., m.p. 325° (block) after softening at 270° and darkening at 320°, [α]_D²² —101°/d in abs. EtOH (*hydrochloride*; *hydrobromide*), which could not be catalytically hydrogenated. *isobromodihydrostrychnine* II is reduced (H₂-PtO₂-H₂O) to a substance, m.p. about 305°, [α]_D²⁰ —265°/d in CHCl₃, which gives an amorphous *methiodide*; the *perchlorate*, *hydrochloride*, and *sulphate* are amorphous or freely sol. H. W.

Biuret reaction. VI. Protein-alkali-heavy metal compounds. H. JESSERER and F. LIEBEN

(Biochem. Z., 1938, 297, 369—378; cf. A., 1937, II, 478).—Zn, Hg^{II}, Mn, Bi, Cd, U, Ti, Cr, Pb, Al, and Sn do not combine with caseinogen (I) in aq. NaOH but Au and Co yield compounds containing respectively Au 10.3, Na 2.0, and N 11.17% and Co 3.21, Na 4.7, and N 11.3%. The at. ratio Cu : Au in the Cu and Au compounds of (I) is 3 : 1 and the Au compound takes up 67% of the Cu taken up by an equiv. amount of (I). Nascent H removes Au and Cu from combination with (I) without affecting the power of the protein to recombine with metals.

W. McC.

Preparation and properties of thyroxyl derivatives of proteins. R. F. CLUTTON, C. R. HARRINGTON, and M. E. YUILL (Biochem. J., 1938, 32, 1119—1132).—See A., 1938, III, 854. The following are described : *N-carbobenzoyloxy-3 : 5-di-iodothyronine Me ester*, m.p. 164.5°; *N-carbobenzoyloxythyronyl-hydrazide*, m.p. 141°, *azide*, amorphous, and *-globulin*, and *N-carbobenzoyloxythyroxyl-albumin* and *-globulin*.

A hæmoglobin from bile pigment. R. LEMBERG, J. W. LEGGE, and W. H. LOCKWOOD (Nature, 1938, 142, 148—149).—Special treatment of a hæmoglobin-ascorbic acid solution yields a new "hybrid" hæmoglobin, now named *choleglobin* (I), which combines reversibly with O₂ or CO. The prosthetic group of (I) is an Fe-bile pigment compound closely related to verdohæmatin. L. S. T.

Hæmocuprein, a copper-protein compound of red blood-corpuscles. T. MANN and D. KEILIN (Nature, 1938, 142, 148).—The isolation of bluish crystals of a Cu-protein compound, now named *hæmocuprein* (I) (N 14.35, S 1.12, Cu 0.34%), from the red blood-corpuscles of ox is described. In serum the Cu is also present as a blue Cu-protein compound similar to, if not identical with, (I). L. S. T.

Micro-analytical practice. E. ABRAHAMCZIK and F. BRÜMEL (Mikrochem., 1938, 24, 268—277).—Various precautionary modifications in apparatus for org. microanalysis are described. A reagent-bottle with pipette sealed into a ground-over stopper, and a ground-over wash-bottle head, are described.

E. W. W.

Micro-technique of organic qualitative analysis. F. SCHNEIDER and D. G. FOULKE (Ind. Eng. Chem. [Anal.], 1938, 10, 445—447).—An extension and elaboration of the capillary and schlieren methods for solubility determination previously described (A., 1938, I, 209). F. N. W.

Determination of carbon and nitrogen in organic compounds by vacuum combustion. Application of this method in soil analysis. N. P. PENTSCHKEV (Z. anal. Chem., 1938, 113, 431—438).—An apparatus is described which enables the sample to be heated in a vac. with CuO, the gases evolved being circulated a few times over a heated CuO spiral, heated Cu gauze, and then P₂O₅ and finally being collected over Hg. The vol. of CO₂ + N₂ having been determined, the gases are further circulated over soda-lime and P₂O₅ and measured again over Hg. The method can be used for the combustion of ordinary org. compounds but is especially applicable to determination of C and N in

soils. The error due to $\text{CO}_3^{''}$ present in the soil is corr. for either by pretreatment with H_3PO_4 or by a separate $\text{CO}_3^{''}$ determination. J. W. S.

Colorimetric determination of ammonia with phenol and hypochlorite.—See A., 1938, I, 534.

Determination of sulphur by means of oxidising alkali melts.—See A., 1938, I, 533.

Constant-temperature bath for Stodola's acetylation micro-apparatus. H. G. CASSIDY (Ind. Eng. Chem. [Anal.], 1938, 10, 456).—The usual glycerol bath is replaced by an enclosed water-bath with reflux, containing a pocket sufficiently large to hold the micro-flask dipping in glycerol. F. N. W.

Determination of alkoxy by the method of Vieböck and Schwappach. S. KINSMAN and C. R. NOLLER (Ind. Eng. Chem. [Anal.], 1938, 10, 424).—Difficulty experienced in applying the method (A., 1931, 107) is shown to be due to the fact that the recommended amount of Br is insufficient to oxidise all the IBr to HIO_3 . When about twice the amount stated is used, accurate results are obtained.

F. N. W.

Micro-determination of deuterioethyl alcohol. K. HANSEN and O. DYBING (Biochem. Z., 1938, 298, 110—114).—The results of a large no. of determinations of $\text{C}_2\text{D}_5\cdot\text{OD}$ by Hansen and Lövenskiöld's modification (Norsk. Mag. Laegevidensk., 1934, 387) of Widmark's method (A., 1922, ii, 789) show that the empirically determined factor (1.170 ± 0.002) to be used in the calculation is approx. 10% below the theoretical val. When 0.01N aq. $\text{Na}_2\text{S}_2\text{O}_3$ is used for titration 0.01 c.c. is equiv. to $1.17 \mu\text{g.}$ of $\text{C}_2\text{D}_5\cdot\text{OD}$.

W. McC.

Determination of oxalic acid. A. LEULIER and J. DORCKE (Bull. Soc. Chim. biol., 1938, 20, 939—946).— $\text{H}_2\text{C}_2\text{O}_4$ can be removed from pure aq. solutions or complex solutions containing other org. acids, $\text{CO}(\text{NH}_2)_2$, etc. by extraction with Et_2O for 72 hr., and determined as oxalate with a max. error of ~5%, where the concn. is 15—35 mg. per l. A similar technique can be applied to urine provided that the p_{H} is maintained at 4—5 during the final pptn. in the presence of COMe_2 to prevent contamination with urinary pigments.

P. G. M.

Determination of formaldehyde in dilute solutions and in the presence of interfering substances. O. HEIM (Ind. Eng. Chem. [Anal.], 1938, 10, 431).—To 10 c.c. of the aq. or aq.-EtOH solution (after 4 or 5 extractions with Et_2O -light petroleum) are added in rapid succession 100 c.c. of 0.1N- AgNO_3 , 1 c.c. of 37% aq. HCl, and 3 c.c. of 25% aq. NaOH. After shaking for 10 min., the mixture is filtered, the ppt. washed with hot dil. HNO_3 and then with hot H_2O , and the filtrate and combined washings are titrated with 0.1N- NH_4CNS using Fe^{III} alum indicator.

F. N. W.

Absorption spectrum of diacetyl.—See A., 1938, I, 492.

Manometric determination of amino-acids with ninhydrin in the Warburg apparatus. C. SCHLAYER (Biochem. Z., 1938, 297, 395—397; cf.

Van Slyke and Dillon, A., 1938, II, 211; Mason, *ibid.*, 252).—Warburg's apparatus is slightly modified, the NH_2 -acid-ninhydrin (with KH_2PO_4 added) being boiled for 3 min. in the reaction vessel which is at 140° . If the vessel is not heated, the process takes several hr., but removal of any proteins present is then unnecessary.

W. McC.

Microdetermination of thiocynoacetic acid. J. V. DUBSKÝ and V. ŠINDELÁŘ (Mikrochem., 1938, 24, 264—267).—The dark violet ppt. from $\text{NCS}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ and aq. CuCl_2 is a $\text{Cu}^{\text{I}}\text{-Cu}^{\text{II}}$ derivative, $\text{Cu}^{\text{I}}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{Cu}^{\text{II}}\cdot\text{OH}\cdot 5\text{H}_2\text{O}$, of $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and in the absence of the latter may be used for the detection or determination of $\text{NCS}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. With CdSO_4 , the salt $(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2)\cdot\text{Cd}$ is obtained.

E. W. W.

Diazo-colour reactions. K. E. JACKSON and W. M. DEHN (J. Amer. Pharm. Assoc., 1938, 27, 576—578).—The substance is treated with AcOH and NaNO_2 and aq. NH_3 then added. The colours resulting from these two stages of the diazo-reaction, together with that of silk on which the colour is fixed, are tabulated for a series of pharmaceutical substances.

F. O. H.

Gravimetric determination of the naphthols with formaldehyde. A. CASTIGLIONI (Z. anal. Chem., 1938, 113, 428—430).—The $\text{C}_{10}\text{H}_7\cdot\text{OH}$ is dissolved in a min. of 95% EtOH and the solution diluted with H_2O . An aliquot portion is treated with CH_2O and HCl, and heated for 3 hr. at 100° . The initially formed white ppt. [probably $\text{CH}_2(\text{C}_{10}\text{H}_6\cdot\text{OH})_2$] turns red-brown or rose coloured according as α - or β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ is used. The ppt. is collected, washed, and dried at 100° . The final products are $\text{OH}\cdot\text{CH}(\text{C}_{10}\text{H}_6\cdot\text{OH})_2$ and $\text{CH}_2\langle\text{C}_{10}\text{H}_6\text{O}\rangle_2$ with α - and β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$, respectively. The method is not applicable to the analysis of a mixture of α - and β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$.

J. W. S.

Methenamine [hexamethylenetetramine] as a qualitative reagent. K. E. JACKSON and W. M. DEHN (J. Amer. Pharm. Assoc., 1938, 27, 578—579).—The colour reactions given by $(\text{CH}_2)_6\text{N}_4$ (0.1 g. in 80 c.c. of conc. H_2SO_4) for various alkaloids, phenols, and other pharmaceutical substances are described.

F. O. H.

Colorimetric determination of equilenin and dihydroequilenin. W. MARX and H. SOBOTKA (J. Biol. Chem., 1938, 124, 693—698).—The alcoholic hormone solution (1.5 c.c.) is mixed in a 15-c.c. centrifuge tube with 1 c.c. of the reagent [10 mg. of diazotised *p*-nitrobenzenecazodimethoxyaniline (K salt) in 10 c.c. of H_2O] and 0.01N- Na_2CO_3 is added. After 1 hr. at room temp. the mixture is centrifuged and the supernatant liquid with excess of the reagent is poured off. The pptd. dye is dried, dissolved in C_6H_6 + EtOH, and determined colorimetrically in the blue solution. (Estrone, œstriol, and œstradiol do not couple readily under similar conditions. If more alkali is added to hasten the sluggish reaction, uncontrollable side reactions prevent the reproducible development of a suitable tint. The test indicates the complete absence of equilenin or dihydroequilenin from human pregnancy urine.

H. W.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

NOVEMBER, 1938.

Rôle of free radicals in elementary organic reactions. F. O. RICE and E. TELLER (J. Chem. Physics, 1938, 6, 489—496).—The principle of least motion, which states that there shall be least change in at. position and in electronic configuration during an elementary reaction, is outlined and is used to discuss the primary reactions between radicals and org. mols. Alkyl radicals will attack most easily exposed positive atoms (in org. substances, H) but will attack exposed negative atoms (N, O, Cl) with difficulty. A completely shielded C should not be attacked but a doubly or triply linked C can react with a radical. The mechanisms of decomp. of different types of mols. are discussed, and the conditions under which org. reactions proceed through radical chains are considered. W. R. A.

Primary decomposition of ethane; and the reaction between ethane and nitric oxide.—See A., 1938, I, 577.

Hydrogenation of ethylene and partly deuteriated ethylene.—See A., 1938, I, 525.

Selective hydrogenation of ethylenic compounds.—See A., 1938, I, 526.

Polymerisation of isobutene.—See A., 1938, I, 523.

Polymerisation of acetylene by slow electrons.—See A., 1938, I, 580.

Ozonisation of Δ^2 -heptinene, phenylacetylene, and diphenylacetylene; the ozonides and their products of evolution. H. PAILLARD and C. WIELAND (Helv. Chim. Acta, 1938, 21, 1356—1366).—One mol. of O_3 is added for each triple linking of a substituted C_2H_2 , giving a very unstable ozonide which rapidly undergoes stabilisation. One of the possible products which best explains the reactions would be a mixed anhydride but this theory does not appear applicable to $CPh:CH$. At $2-3^\circ$ Δ^2 -heptinene in CCl_4 absorbs the theoretical amount of O_3 but the product when decomposed by H_2O gives less than the expected amounts of hexoic acid (I) and, particularly, of HCO_2H ; CO is produced. With $SOCl_2$ the ozonide yields $C_5H_{11}\cdot COCl$, CO , HCl , and SO_2 . The ozonide formed in $EtCl$ at -80° gives (I) and CO but not HCO_2H when the temp. rises; when hydrolysed by $COMe_2\cdot H_2O$ at -80° it yields (I), CO , and H_2O but not HCO_2H . $CPh:CH$ slowly absorbs 1 mol. of O_3 and the ozonide when hydrolysed gives a deficiency of $BzOH$ and particularly of HCO_2H ; its formation is accompanied by the appearance of viscous products on the walls of the vessel.

C_2Ph_2 gives an ozonide from which only $BzOH$ could be obtained on hydrolysis; the yield was moderate.

H. W.

Concentration of chlorine isotopes [in carbon tetrachloride].—See A., 1938, I, 581.

Reactions of fluorinated derivatives with sodium, potassium, and magnesium. A. L. HENNE (J. Amer. Chem. Soc., 1938, 60, 2275—2276).—Fluorides do not give the Wurtz or Grignard reactions. Addition of $CH_2I\cdot CHF_2$ (I) to Mg in Et_2O may give a trace of unstable Mg derivative, but the main products are $CH_2\cdot CHF$, MgF_2 , and MgI_2 . $CH_2Br\cdot CHF_2$ (II) does not react with Mg . Na or K removes one atom of each halogen from (I) or (II), but CCl_3F_2 , $CHClF_2$, and $CHBrF_2$ do not react. R. S. C.

Tertiary butyl chloride from tertiary amyl chloride and hydrogen fluoride. J. H. SIMONS, G. H. FLEMING, F. C. WHITMORE, and W. E. BISSINGER (J. Amer. Chem. Soc., 1938, 60, 2267—2269).— CMe_2EtCl and 1 mol. of anhyd. HF at 0° give 10—17% of Bu^tCl with, probably, hexyl, heptyl, decyl and/or undecyl, and pentadecyl chloride. R. S. C.

Preparation of chlorides from aliphatic branched-chain secondary carbinols. F. C. WHITMORE and F. JOHNSTON (J. Amer. Chem. Soc., 1938, 60, 2265—2267).— $CHMePr^s\cdot OH$ with $ZnCl_2\cdot HCl$ at -10° , $SOCl_2\cdot C_5H_5N$ at 20° , PCl_5 at $0-30^\circ$, or gaseous HCl at 20° gives CMe_2EtCl ; PCl_3 gives a phosphite. $CHEtPr^s\cdot OH$, $CHPr^s\cdot OH$, and $CHPr^s\cdot OH$ with gaseous HCl give similarly CMe_2Pr^sCl , CMe_2Bu^sCl , and CMe_2Bu^sCl , respectively. However, $CHMeBu^s\cdot OH$, $iso-C_5H_{11}\cdot CHMe\cdot OH$, and $CH_2Bu^s\cdot CHMe\cdot OH$ with gaseous HCl give the chlorides without rearrangement. The effect of branching at C in the α -position to the OH is thus clear-cut.

R. S. C.

Organic syntheses by means of sunlight. E. OLIVERI-MANDALÀ (Chim. e l'Ind., 1938, 20, 535—538).—A review, including recent work (A., 1938, II, 361).

E. W. W.

Action of the alkaline-earth oxides on alcohols. E. BERNER (Ber., 1938, 71, [B], 2015—2021).—Anhyd. $MeOH$ when kept at room temp. or distilled over CaO becomes partly hydrated owing to the reactions $CaO + MeOH = Ca(OH)\cdot OMe$ (I) and $(I) + MeOH \rightleftharpoons Ca(OMe)_2 + H_2O$. By reason of their greater solubility the changes with SrO and BaO are somewhat more complex. Thus, dependent on temp., the reaction $Sr(OMe)_2 + 2H_2O \rightarrow Sr(OH)_2 + 2MeOH$ can also occur. CaO reacts very slowly with boiling anhyd. $EtOH$ whereas SrO and BaO give

respectively an immediate slight and marked evolution of heat. Allyl alcohol gives a perceptible heat evolution with CaO; this is very marked with SrO and BaO. $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$ appears to evolve heat only with BaO whilst $\text{CH}_2\text{Ph}\cdot\text{OH}$ does not appear to react with any of the oxides at room temp. When exposed to moist air in the absence of CO_2 (I) reacts thus: $(\text{I}) + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{MeOH}$. At 450° (I) evolves H_2 mixed with a little CH_4 and sometimes CO while CaO and CaCO_3 remain. Similar gaseous mixtures are obtained from the products of MeOH and SrO or BaO. H. W.

Purification of organic solvents [propyl alcohol].—See A., 1938, I, 537.

Constitution of the alcohol (δ -methyl- Δ^8 -penten- β -ol) previously described as $\alpha\gamma$ -trimethylallyl alcohol. J. KENYON and D. P. YOUNG (J.C.S., 1938, 1452—1454).—Mg β -methylallyl chloride and MeCHO afford *dl*- δ -methyl- Δ^8 -penten- β -ol (I) (*dl*-*p*-xenylurethane, m.p. $64-65^\circ$), identical with the compound obtained by Duveen and Kenyon (A., 1936, 1486) from $\alpha\gamma$ -trimethyltrimethylene glycol (II). Crystallisation from COMe_2 of the brucine salt, m.p. $81.5-82^\circ$, of the *dl*-H phthalate affords a residue decomposed to the (+)(I) H phthalate, m.p. $42-43^\circ$, $[\alpha]_{5461}^{20} +18.1^\circ$ in EtOH, hydrolysed to (+)(I), b.p. $42^\circ/15$ mm. (many vals. of $[\alpha]$ in CS_2 and C_6H_6). The COMe_2 mother-liquor affords a residue which when crystallised from MeOH gives the brucine salt, m.p. $79-82^\circ$ (decomp.), $\alpha_{5461} -18.0^\circ$ in CHCl_3 , of the (–)(I) H phthalate, decomposed to the (–)(I) H phthalate, m.p. $42-43^\circ$, $[\alpha]_{5461} -17.6^\circ$ in EtOH. Complete dehydration of (II) and also further dehydration of the hexenol obtained as a partial dehydration product affords $\alpha\gamma$ -dimethylbutadiene, also obtained from (I). Dehydration of (II) proceeds: $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH} \rightarrow \text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH} \rightarrow \text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CHMe}$. The ozonide of (I) is decomposed to pentan- β -ol- δ -one, b.p. $64-65^\circ/18$ mm. Parachors of (–)(I) are recorded. A. T. P.

Identification of the isomeric hexanols by their 3 : 5-dinitrobenzoates and their compounds with α -naphthylamine. P. SUTTER (Helv. Chim. Acta, 1938, 21, 1266—1272).—The 3 : 5-dinitrobenzoates are obtained from the hexanols and 3 : 5-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{COCl}$ in C_6H_6 containing anhyd. $\text{C}_5\text{H}_5\text{N}$. The additive compounds of the esters and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ are obtained in 80% EtOH. 3 : 5-Dinitrobenzoates (A) and their additive compounds (B) with $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ of the following are described: hexan- α -ol, A, m.p. $60-61^\circ$, B, m.p. $103-104^\circ$; β -methylpentanol, A, m.p. 50.5° , B, m.p. 60° ; γ -methylpentanol, A, m.p. 38° , B, m.p. 81.5° ; δ -methylpentanol, A, m.p. 72° , B, m.p. 99° ; $\beta\gamma$ -dimethylbutanol, A, m.p. 51.5° , B, m.p. 99° ; $\beta\beta$ -dimethylbutanol, A, m.p. 51° , B, m.p. 107.5° ; $\gamma\gamma$ -dimethylbutanol, A, m.p. 83.5° , B, m.p. 132.5° ; γ -hydroxymethylpentanes, A, m.p. 51.5° , B, m.p. 82.5° ; hexan- β -ol, A, m.p. 38° , B, m.p. 91° ; hexan- γ -ol, A, m.p. 77° , B, m.p. 71.5° ; β -methylpentan- γ -ol, A, m.p. 85° , B, m.p. 72.5° ; δ -methylpentan- β -ol, A, m.p. 65° , B, m.p. 92.5° ; γ -methylpentan- β -ol, A, m.p. 43.5° , B, m.p. 79° ; $\beta\beta$ -dimethylbutan- γ -ol, A, m.p. 107° , B, m.p. 114° ; β -methylpentan- β -ol, A, m.p. 72° , B, m.p. 113° ; γ -methylpentan- γ -ol, A, m.p. 96.5° ,

B, m.p. 85° ; $\beta\gamma$ -dimethylbutan- β -ol, A, m.p. 111° , B, m.p. 137° . H. W.

System sodium molybdate-mannitol in aqueous solution.—See A., 1938, I, 567.

Catalytic dehydrogenation of sugar alcohols. J. W. E. GLATTFIELD and S. GERSHON (J. Amer. Chem. Soc., 1938, 60, 2013—2023).— $\text{PtO}_2\cdot\text{H}_2\text{O}$ oxidises: mannitol stoichiometrically in H_2O at $75-90^\circ$. In air the Pt formed acts as catalyst for further oxidation, the optimum temp. being $80-85^\circ$. Pressures of > 1 atm. are less effective, but, if the PtO_2 is first reduced at 1 atm., later reaction is faster at increased pressure. The temp. ($400-600^\circ$) of prep. of the PtO_2 is without influence. Oxidation is primarily to *d*-mannose (I) and *d*-fructose (II), but further oxidation to *d*-mannonic, *d*-mannuronic, *d*-mannosaccharic, and α -keto-*d*-mannonic acid, and *d*-glucosone occurs. The same further products are obtained from (I) and (II) in separate experiments. The max. amount of (I) formed is 67.7% (64.7% at 1 atm.). The max. yield (17.6%) of pure (I) is obtained by stopping the reaction when 55–60% of reducing material (50% of acid) is present; 32.5% of syrupy (I) is isolated, 35.3% as pure phenylhydrazone, or 19.9% as α -methyl-*d*-mannoside. Dulcitol gives similarly *dl*-galactose (III), -tagatose, -galactonic and -galacturonic acid, α -keto-*dl*-galactonic and mucic acid, and *d*-tagatose. The optimum yield of cryst. (III) is 15.5%, or 30% as phenylhydrazone. Analysis of the products is effected partly by titration with NaOH, I, and Benedict's solution, and partly by isolation of cryst. products. *dl*-Galactose-2 : 4-dibromophenylhydrazone melts at $171-172^\circ$ (corr.). The osazone and phenylhydrazone of *dl*-galactose decompose at $152-153^\circ$ (corr.) and $208-209^\circ$ (corr.), respectively. *d*-Mannosephenylhydrazone melts at $195-196^\circ$ (corr.). R. S. C.

New syntheses of *l*-galomethylitol and *d*-rhamnitrol. K. GÄTZI and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 914—925).—*d*-Arabinose Et_2 mercaptal, m.p. $129-129.5^\circ$ (corr.), is converted by COMe_2 and anhyd. CuSO_4 at room temp. into 4 : 5-isopropylidene-arabinose Et_2 mercaptal, m.p. $75-76^\circ$ (corr.), $[\alpha]_D^{20} -7.4^\circ \pm 2^\circ$ in MeOH, or by more prolonged treatment into (?) 2 : 3 : 4 : 5-diisopropylidene-arabinose Et_2 mercaptal, b.p. $110^\circ/0.2$ mm., $[\alpha]_D^{20} +57.8^\circ \pm 2^\circ$ in MeOH. This is converted by HgCl_2 and pptd. CdCO_3 in COMe_2 at room temp. into 2 : 3 : 4 : 5-diisopropylidene- α -*d*-arabinose (I), b.p. $84^\circ/0.05$ mm., $[\alpha]_D^{20} -34.5^\circ \pm 1^\circ$ in CHCl_3 , which strongly reduces $\text{NH}_3\text{-Ag}_2\text{O}$ and becomes partly polymerised when kept. It is oxidised ($\text{KMnO}_4\text{-KOH}$) to diisopropylidene-*d*-arabonic acid, m.p. $84-85.5^\circ$, $[\alpha]_D^{20} +20.9^\circ \pm 1.5^\circ$ in COMe_2 (K salt, $[\alpha]_D^{20} +19.9^\circ \pm 1^\circ$ in H_2O). MgMeBr and (I) give a product, b.p. $81^\circ/0.4$ mm., which is separated by treatment with cold pentane into diisopropylidene-*d*-rhamnitrol, m.p. $66.5-67^\circ$, $[\alpha]_D^{20} +1^\circ \pm 1.5^\circ$ in MeOH, and diisopropylidene-*l*-galomethylitol, $[\alpha]_D^{20} +3.0^\circ \pm 2^\circ$ in MeOH. Hydrolysis of the COMe_2 derivatives leads to *l*-galomethylitol, m.p. $105-106^\circ$ (corr.), $[\alpha]_D^{20} +20.6^\circ \pm 2^\circ$ in MeOH, and *d*-rhamnitrol, m.p. $102-104^\circ$ (corr.), or, after preservation, m.p. $122-123^\circ$ (corr.), $[\alpha]_D^{20} -11.5^\circ \pm 1.5^\circ$ in H_2O . *l*-Rhamnitrol, prepared for comparison,

had m.p. 122.5—123° (corr.), $[\alpha]_D^{25} + 12.0^\circ \pm 1^\circ$ in H_2O . *dl*-Rhamnitol has m.p. 112—115°. *d*-Talomethylitol (II), m.p. 110.5—111° (corr.), is obtained according to the sequence: *d*-galactose \rightarrow diisopropylidene-*d*-galactose \rightarrow diisopropylidene-*d*-galactose *p*-toluenesulphonate \rightarrow 6-iododiisopropylidene-*d*-galactose \rightarrow (by Raney Ni in MeOH) \rightarrow diisopropylidene-*d*-fucose \rightarrow Ba *d*-fuconate \rightarrow talomethylonolactone \rightarrow (II). H. W.

Twitchell's reagent. II. Twitchell's reagent as catalyst in the preparation of acetals. J. N. ZAGANIARIS (Ber., 1938, 71, [B], 2002—2005; cf. A., 1936, 1487).—Granulated $CaCl_2$ added gradually to a mixture of CH_2O and excess of MeOH containing Twitchell's reagent at 0° gives $CH_2(OMe)_2$ in 50% yield. $CH_2(OEt)_2$ and $CHMe(OEt)_2$ are obtained in 40% and 50% yield, respectively, whilst the yields of heptaldehyde Me_2 acetal, b.p. 164—165°, and the corresponding Et_2 acetal are 62.5% and 64%, respectively. $PhCHO$ could not be etherified but *o*-, *m*-, and *p*- $NO_2 \cdot C_6H_4 \cdot CHO$ give the corresponding Me_2 acetals in 60%, 70%, and 30% yield. 65%, 68%, and 30% yields of *o*-, *m*-, and *p*-nitrobenzaldehyde Et_2 acetal, b.p. 153—155°/6 mm., are obtained. Glycol formal and heptaldehyde C_2H_4 acetal are derived in 30% and 25% yield from $(CH_2OH)_2$ and CH_2O or *n*- $C_5H_{11}CHO$, respectively. Benzil glycol diacetal is obtained. H. W.

Ether-like compounds. I. Preparation of acetals and ketals. E. I. SALMI (Ber., 1938, 71, [B], 1803—1808).—In the prep. of acetals and ketals, it is advantageous to remove the H_2O formed as a ternary mixture. Reaction then proceeds nearly to completion, only a small amount of catalyst is required, and the product is immediately anhyd. and can be freed from the catalyst by distillation in a vac. Special types of apparatus are figured for the cases when the H_2O produced is lighter or heavier than the remaining distillate and when a desiccating agent must be used. The method is useless when the aldehydes or alcohols have such a low b.p. that they constitute the bulk of the distillate. The following are described: ethylene, b.p. 99.5—101.0°/17—18 mm., $\alpha\beta$ -propylene, b.p. 84.6—85°/6 mm., trimethylene, b.p. 95.0—95.3°/4 mm., and $\alpha\gamma$ -butylene, b.p. 100.1—101.0°/6 mm., ketals of $CH_2Ac \cdot CO_2Et$; cyclopentanone ethylene, b.p. 57.0—57.2°/18 mm., $\alpha\beta$ -propylene, b.p. 61.8—62.4°/18 mm., trimethylene, b.p. 62.8—63.0°/7 mm., and $\alpha\gamma$ -butylene, b.p. 77.0—77.4°/12.5 mm., ketal; cyclohexanone ethylene, b.p. 73°/16 mm., $\alpha\beta$ -propylene, b.p. 76.0—76.8°/15 mm., trimethylene, b.p. 91.5—93.0°/16 mm., and $\alpha\gamma$ -butylene, b.p. 92.0—92.8°/14 mm., ketal; the cyclohexanone ketal of hexahydro-pyrocatechol, $CH_2 \begin{smallmatrix} \diagup CH_2 \cdot CH_2 \diagdown \\ \diagdown CH_2 \cdot CH_2 \diagup \end{smallmatrix} C \begin{smallmatrix} \diagup O \cdot CH \cdot CH_2 \cdot CH_2 \diagdown \\ \diagdown O \cdot CH \cdot CH_2 \cdot CH_2 \diagup \end{smallmatrix}$, b.p. 105.0—106.1°/4 mm., and of Et_2 *d*-tartrate, $CH_2 \begin{smallmatrix} \diagup CH_2 \cdot CH_2 \diagdown \\ \diagdown CH_2 \cdot CH_2 \diagup \end{smallmatrix} C \begin{smallmatrix} \diagup O \cdot CH \cdot CO_2Et \diagdown \\ \diagdown O \cdot CH \cdot CO_2Et \diagup \end{smallmatrix}$, b.p. 160.0—161.3°/3 mm.; 1-menthone ethylene ketal, b.p. 114.3—116.2°/18 mm.; the 1-menthone ketal of pyrocatechol, b.p. 140.8—141.7°/6 mm.; ethylene ketal of synthetic camphor, b.p. 109.0—111.2°/15 mm. H. W.

Keten acetals. III. Bromination of bromoketen diethyl acetal. Other halogenated keten

acetals. A. MAGNANI and S. M. McELVAIN (J. Amer. Chem. Soc., 1938, 60, 2210—2213; cf. A., 1938, II, 4).— $CHBr \cdot C(OEt)_2$ (I) at 0—5° absorbs only 0.68 mol. of Br and no further absorption then occurs at 25°; slightly >50% reacts thus: (I) + $Br_2 \rightarrow CHBr_2 \cdot CBr(OEt)_2 \rightarrow CHBr_2 \cdot CO_2Et$ (II) + $EtBr$; slightly <50% reacts thus: 2(I) + $Br_2 \rightarrow CHBr_2 \cdot C(OEt)_2 \cdot CHBr \cdot CBr(OEt)_2 \rightarrow EtBr + CHBr_2 \cdot C(OEt)_2 \cdot CHBr \cdot CO_2Et$ (III) $\rightarrow CBr_3 \cdot C(OEt)_2 \cdot CH_2 \cdot CO_2Et$; a small amount of the reaction, (II) + (III) $\rightarrow CBr_3 \cdot CO_2Et + CHBr_2 \cdot C(OEt)_2 \cdot CH_2 \cdot CO_2Et$, also occurs. Chloro-, b.p. 166°/732—740 mm., dichloro-, b.p. 177°/732—740 mm., and dibromo-, b.p. 206—208°/732—740 mm., -keten Et_2 acetal are prepared from the halogenated acetaldehyde acetals by $KOBu^+$. $CHCl_2 \cdot CH(OEt)_2$ is obtained from anhyd. $CHMe(OEt)_2$ and Cl_2 at 34—36°, but not by Fritsch's method (A., 1894, i, 483). $CCl_3 \cdot CH(OEt)_2$ is obtained from $CCl_3 \cdot CHCl \cdot OEt$ and abs. $EtOH$, but this method does not give $CBr_3 \cdot CH(OEt)_2$ (IV). 2—15% of (IV) is obtained by adding Br to boiling $CHBr_2 \cdot CH(OEt)_2$, 15% of $(CHBr_2 \cdot CO_2Et + EtBr + HBr)$ and >45% of $(CBr_3 \cdot CHO + EtBr)$ being also obtained. The b.p. of keten acetals are 20—24° > those of the corresponding esters. R. S. C.

Esters of pyrocarbonic acid. T. BOEHM and D. MEHTA (Ber., 1937, 71, [B], 1797—1802).—Agitation of emetine hydrochloride (I) and $ClCO_2Et$ in $CHCl_3$ with 10% aq. KOH at room temp. gives carbethoxymetine (II) and Et_2 pyrocarbonate (III), b.p. 85°/12 mm., with a little Et_2CO_3 . (I) may be replaced by (II), quinine, carbethoxyquinine, codeine, narcotine, isokairoline, or $NPhMe_2$ but not by NH_2Ph , $NHPhMe$, piperidine, or tetrahydroquinoline. A *tert*. N appears essential. When heated (III) gives CO_2 and Et_2CO_3 . It is immediately hydrolysed by KOH in abs. $EtOH$ to $KEtCO_3$. With $N_2H_4 \cdot H_2O$ it yields $(NH \cdot CO_2Et)_2$, m.p. 135°. Similarly $ClCO_2Pr^a$ affords Pr^a_2 pyrocarbonate, b.p. 100°/13 mm., which passes when heated into $Pr^a_2CO_3$ and is transformed by $N_2H_4 \cdot H_2O$ into Pr^a_2 hydrazinedicarboxylate, m.p. 63—64°. The corresponding Me_2 ester loses CO_2 and passes into Me_2CO_3 when distilled in vac. The course of the changes is probably: $N + ClCO_2R \rightarrow NCl \cdot CO_2R$ (IV), $2(IV) + H_2O = 2:NHCl + O(CO_2R)_2$. The following examples of the uses of (III) as acylating agent are recorded: NH_2Ph and $NHPhMe$ are transformed at room temp. into the corresponding urethanes; *m*- $NH_2 \cdot C_6H_4 \cdot CO_2H$ at 100° gives *m*-carbethoxyaminobenzoic acid, m.p. 190°; *p*- $NH_2 \cdot C_6H_4 \cdot CO_2H$ yields *p*-carbethoxyaminobenzoic acid, m.p. 204—205°, or *p*-carbethoxyaminobenzoic anhydride if the action is prolonged; $PhOH$ and quinol at 100° yield carbethoxyphenol, b.p. 112°/17 mm., and dicarbethoxyquinol, m.p. 101—102°, respectively; *p*- $NH_2 \cdot C_6H_4 \cdot OH$ is transformed into $CO_2Et \cdot O \cdot C_6H_4 \cdot NH \cdot CO_2Et$, m.p. 108—109°. *N*-Carbethoxymetine perchlorate has m.p. 254°. H. W.

Formation of salts from graphite by strong acids.—See A., 1938, I, 531.

Method of distinguishing primary, secondary, and tertiary aliphatic acids. F. C. WHITMORE and H. M. CROOKS, jun. (J. Amer. Chem. Soc., 1938,

60, 2078—2079).—Fifteen further examples (cf. Laughlin *et al.*, A., 1933, 49) illustrate the rule that with P_2O_5 at 150—160° aliphatic acids $CH_2R\cdot CO_2H$ give 1·1—0% of CO and 0·77—13% of CO_2 , whereas acids $CHRR'\cdot CO_2H$ give 8·8—30% of CO and 1·7—0·5% of CO_2 , and acids $CR'R''\cdot CO_2H$ give 55—90% of CO and 0—0·2% of CO_2 . R. S. C.

Photochemical polymerisation of methyl acrylate vapour.—See A., 1938, I, 579.

Electrolysis of mixtures of nitrates with salts of methylethylacetic acid. F. FICHTER and P. SUTTER (Helv. Chim. Acta, 1938, 21, 1401—1407).—Electrolysis of a solution 4N in $CHMeEt\cdot CO_2Na$ and 2N in $NaNO_3$ yields as main products $CHMe\cdot CHMe$ and $CHEt\cdot CH_3$, but these are in part decomposed further to yield $(CHMe\cdot NO_2)_2$, Bu^sNO_3 , Bu^sOH , and $COMeEt$, as well as traces of a higher alcohol ($C_8H_{17}\cdot OH$ or $C_{10}H_{21}\cdot OH$) and a higher glycol.

J. W. S.

Addition of hydrogen bromide to undecenoic acid in toluene solution. III. Influence of impurities in undecenoic acid on the effects of oxygen and of reduced nickel. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1938, 13, 574—577; cf. A., 1938, II, 216).—HBr and impure undecenoic acid (from castor oil) yield 8% of the κ -Br-acid (I) (proportion determined by the m.p.). In presence of limited amounts of O_2 the impure acid gives a much greater proportion of (I) than the pure, but with reduced Ni the impurities have no effect.

A. LI.

Water-oil emulsions. I. Preparation of anhydrous magnesium oleate. R. C. PINK (J.C.S., 1938, 1252—1254).—The prep. of Mg oleate and of its hydrate is described. Addition of small amounts of H_2O to solutions of the anhyd. soap in C_6H_6 ppts. the soap in an insol. form containing H_2O , but not as a true emulsion. In the inversion of oil-in- H_2O emulsions with $MgCl_2$ the Mg oleate formed does not dissolve in the oil phase.

O. J. W.

Optical properties of fermentation lactic acids.—See A., 1938, III, 960.

Enol content of some β -keto-esters. A. B. NESS and S. M. McELVAIN (J. Amer. Chem. Soc., 1938, 60, 2213—2215).—The enol content, determined by Br in 0·1M solution in hexane, lies between 46·4 and 59·4% for 7 esters, $CH_2Ac\cdot CO_2R$, and between 1·8 and 10·2% for 10 esters, $CHRAc\cdot CO_2Et$ or $CH_2R\cdot CO\cdot CHR'\cdot CO_2Et$ (R and R' = alkyl). Certain regularities are noted.

R. S. C.

Ozonisation of maleic and fumaric acids and various derivatives of these acids. E. BRINER and D. FRANK (Helv. Chim. Acta, 1938, 21, 1297—1312).—Esters of maleic, fumaric, mesaconic, citraconic, and itaconic acids yield relatively stable ozonides in org. solvents (CCl_4 , $AcOH$). These ozonides split normally, yielding acids and aldehydes or ketones. The acids and their Na salts in aq. solution yield unstable ozonides which decompose as they are formed, the main products being CO_2 and CH_2O . This premature decomp. can be retarded by ozonation in MeOH at -60°.

J. W. S.

Preparation and toxicity of menthyl hydrogen succinate and its heavy-metal salts. W. M. LAUTER and V. L. VRLA (J. Amer. Pharm. Assoc., 1938, 27, 753—755).—The following salts were prepared: *Bi* (min. lethal dose intramuscularly in rats approx. 200 mg. of Bi per kg.); *basic Bi*, m.p. 206° (decomp.); *Mn*, m.p. 168—170°; *Ag*, m.p. 104°; *HgCl adduct*. The Bi and Mn salts are sol., and the Ag and Hg salts insol., in vegetable oils. F. O. H.

Decomposition of citric acid by ferric iron. S. I. PELTZ and E. V. LYNN (J. Amer. Pharm. Assoc., 1938, 27, 774—776).—Exposure to sunlight of aq. citric acid- $Fe(OH)_3$ preps. yields CO_2 , whilst Fe^{+++} is completely reduced to Fe^{++} ; $COMe_2$ and CH_2O could not be detected but distillates give a CHI_3 , but not nitrosopruesside, reaction. Alkali citrates are stable under similar conditions.

F. O. H.

Aërobic formation of citric acid from acetic acid by yeast. R. SONDERHOFF and M. DEFFNER (Annalen, 1938, 536, 36—43; cf. Wieland and Sonderhoff, A., 1933, 32).—Citric acid (I) is obtained in very small yield by the action of impoverished yeast on $NaOAc$ or $KOAc$ in about 2% and 20% yield from $Ca(OAc)_2$ and $Ba(OAc)_2$. The function of Ba^{++} , which also restricts the O_2 absorption, is to ppt. (I) as the very sparingly sol. Ba salt. This view is confirmed by the observation that the yields of (I) increase in more conc. solution and at p_H 7—7·4. Reaction proceeds less readily with fresh than with impoverished yeast and the concn. of $AcOH$ which can be dehydrogenated varies with the yeast. There is invariably a short period of induction. The best yields are obtained at p_H 7—7·4. Addition of small amount of KH_2PO_4 (or NH_4NO_3) often considerably increases the rate of reaction but diminishes the yield of (I) somewhat. Although addition of *l*-malic acid (II) invariably increases the yield of (I) and permits limited reaction with otherwise inactive yeasts it does not appear probable that (I) is formed by dehydrogenation of (I)+(II). $EtOH$ greatly increases the amount of $AcOH$ which enters into reaction; the yield of (I) remains unchanged whereas that of succinic acid is greatly increased. Oxalacetic acid (III) frequently accelerates the dehydrogenation of $AcOH$ and increases the yield of (I) up to 50%. $AcCO_2H$ and (III) give the compound $CO_2H\cdot CH_2\cdot C(OH)(CO_2H)\cdot CH_2\cdot CO\cdot CO_2H$ even in the absence of yeast but there is no evidence of the production of (I).

H. W.

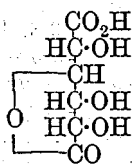
Anaërobic fermentation of citric acid by bacteria. M. DEFFNER (Annalen, 1938, 536, 44—50; cf. Sonderhoff and Deffner, A., 1936, 1560).—Resting or growing bacteria give the same products in about the same amount from citric (I) and oxalacetic (II) acid except that about 1 mol. of $AcOH$ more is formed from (I) than from (II). Since (II) is attacked more rapidly than (I) it is probable that the anaërobic fermentation of (I) occurs through (II) and $AcOH$. Whereas with growing bacteria the relative amounts of products depend greatly on conditions, exact relationships are observed with resting bacteria which render probable the following scheme: $CO_2H\cdot C(OH)(CH_2\cdot CO_2H)_2 = CO_2H\cdot CH_2\cdot CO\cdot CO_2H$ (II) + $AcOH$; (II) + $4H = (CH_2\cdot CO_2H)_2 + H_2O$; $2(II) + 2H_2O - 4H = 4CO_2 + 2AcOH$; (II) + $H_2O =$

$\text{CO}_2 + \text{HCO}_2\text{H} + \text{AcOH}$. A small excess of HCO_2H in certain experiments is due to its production from AcCO_2H . EtOH and traces of MeCHO are also produced. H. W.

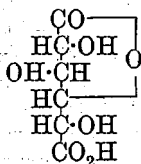
Reactions of ascorbic acid. Colour reactions of alkaloids and sterols. G. WOKER and I. ANTENER (Helv. Chim. Acta, 1938, 21, 1345—1349; cf. A., 1937, ii, 367).—The colour reactions of ascorbic acid distillates with cholesterol, bile acids, piperine, picrotoxin, santonin, veratrine, and morphine are compared with those given by furfuraldehyde.

H. W.

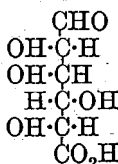
Reduction of the two *d*-saccharolactones by sodium amalgam. M. SUTTER and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 1210—1218).—The prep. of the saccharolactonic acids, m.p. 135° (I) (Schmidt



(I.)



(II.)



(III.)

et al., A., 1938, II, 42, 170) and [(II) hydrate], m.p. about 90°, $[\alpha]_{\text{D}}^{25} +32.5^\circ \pm 0.5^\circ$ to $+29.5^\circ$ in H_2O in 48 hr. (Reichstein *et al.*, A., 1933, 1143), is described. (I) and (II) could not be inter-converted. Reduction of (II) with Na-Hg at 0°, if interrupted when the solution has acquired its max. reducing power towards Fehling's solution, gives *d*-glucuronic acid, m.p. 158—161° (corr.), whilst complete reduction leads to *l*-gulonolactone, m.p. 181—183° (corr.). Similarly, semi-reduction of (I) leads to non-cryst. *galuronic acid* (III) [*phenylhydrazine* salt of the *phenylhydrazone*, m.p. 120—122° (corr.)] and complete reduction gives *d*-gluconic acid [*phenylhydrazide*, m.p. 201—202° (corr.)]. H. W.

Conversion of uronic acids into the corresponding hexoses. V. Transformation of the aldobionic acid (from gum arabic) into the corresponding disaccharide. VI. Configuration of the glucosidic union of the aldobionic acid from gum arabic. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1938, 125, 345—354, 355—367; cf. A., 1938, I, 4, 125).—V. Aldobionic acids are hydrogenated to aldobiosides in presence of $\text{Cu-Cr}_2\text{O}_3$, protective Ac or CMe_2 groups being simultaneously removed. Thus, " β "-methylaldobionide *Me* ester hexa-acetate (prep. by $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$), m.p. 140°, $[\alpha]_{\text{D}}^{25} -54.2^\circ$ in CMe_2 , in MeOH at 175°/3600 lb. gives impure β -methyl-6-glucosidogalactofuranose, $[\alpha]_{\text{D}}^{25} -69.5^\circ$ in H_2O , the nature of which is confirmed by hydrolysis by 0.01N-HCl at 100° in 4 hr. to 6-glucosidogalactofuranose (I), m.p. 126—128°, $[\alpha]_{\text{D}}^{25} +14.2^\circ$ in H_2O . Similarly isopropylidene-6- β -glucuronidogalactose *Me* ester 2:3:4-triacetate, m.p. 162°, $[\alpha]_{\text{D}}^{25} -66.3^\circ$ in CHCl_3 (prep. from the free acid described), in MeOH at 175°/4000 lb. gives isopropylidene-6- β -glucosidogalactose, $[\alpha]_{\text{D}}^{25} -68.7^\circ$ in H_2O , hydrolysed to (I).

VI. The aldobionic acid from gum arabic is shown to contain a β -glucosidic union. With H_2 -Raney Ni in H_2O at 125°/3000 lb. it gives 6-glucuronidodulcitol,

dimorphous, m.p. 179—182° and 132—135°, $[\alpha]_{\text{D}}^{25} -21.7^\circ$ in H_2O [*Me* ester, m.p. about 83—85°, $[\alpha]_{\text{D}}^{25} -27.3^\circ$ in H_2O [octa-acetate (II), m.p. 154—155°, $[\alpha]_{\text{D}}^{25} -31.7^\circ$ in CMe_2]], also obtained impure from 6- β -glucuronidogalactose *Me* ester hepta-acetate. With H_2 -Cu-Cr₂O₃ in MeOH at 175°/4500 lb. (II) gives 6-glucosidodulcitol, $[\alpha]_{\text{D}}^{25} -22.9^\circ$ in H_2O (nona-acetate, m.p. 147—148°, $[\alpha]_{\text{D}}^{25} -29.2^\circ$ in CMe_2). Diisopropylidene-*d*-galactose, bromoacetyl-*d*-glucose, Ag_2O , and anhyd. CaSO_4 in C_6H_6 give a product, which after hydrolysis yields 6- β -glucosido- α -galactose, m.p. 128—130°, $[\alpha]_{\text{D}}^{25} +34.2^\circ \rightarrow +14.7^\circ$ in H_2O , hydrogenated (Raney Ni) in H_2O at 125°/3000 lb. to the alcohol, $+x\text{H}_2\text{O}$, m.p. 129—130°, $[\alpha]_{\text{D}}^{25}$ (anhyd.) -19.5° in H_2O . The alcohol is readily hydrolysed by emulsin; methylation first by $\text{Me}_2\text{SO}_4\text{-NaOH}$ - $\text{H}_2\text{O-CMe}_2$ at 60—100° and then by $\text{MeI-Ag}_2\text{O-CMe}_2$ gives hepta-, m.p. 75—77°, $[\alpha]_{\text{D}}^{25} -25.5^\circ$ in EtOH, and hexa-methyl-6- β -methylglucosidogalactoside, m.p. 119°, $[\alpha]_{\text{D}}^{25} -15.1^\circ$ in EtOH. R. S. C.

Derivatives of *d*-galacturonic acid. IV. Preparation of methyl *d*-galacturonate. V. Synthesis of the methyl esters of cholesterol, sitosterol, and ergosterol triacetate-*d*-galacturonides. H. M. SELL and K. P. LINK (J. Biol. Chem., 1938, 125, 229—233, 235—240; cf. A., 1937, II, 442).—IV. Prep. of *Me d*-galacturonate is improved so as to avoid glucoside formation.

V. *Me* acetobromo-*d*-galacturonate, cholesterol, and Ag_2CO_3 in dry C_6H_6 give *Me* cholesteryl- β -*d*-galacturonide triacetate, m.p. 219—220°, $[\alpha]_{\text{D}}^{25} -6.36^\circ$ in CHCl_3 . *Me* ergosteryl-, m.p. 204—205°, $[\alpha]_{\text{D}}^{25} -27.9^\circ$ in CHCl_3 , and sitosteryl- β -*d*-galacturonide triacetate, m.p. 172—173°, $[\alpha]_{\text{D}}^{25} +1.0^\circ$ in CHCl_3 , are similarly prepared. Hydrolysis gives the free glucosides as insol., amorphous powders that cannot be purified. R. S. C.

Preparation of 3:4:5-trimethyl-*l*-galacturonic acid. R. S. TIPSON (J. Biol. Chem., 1938, 125, 341—345).—2:3:4-Trimethyl-*d*-galacturonic acid, $+ \text{H}_2\text{O}$, m.p. 96—98°, $[\alpha]_{\text{D}}^{25} +126.3^\circ \rightarrow +104.2^\circ$ in 60 min. in H_2O , prepared from the *Me* ester (I) of the methylglucoside by N-HCl at 100°, is hydrogenated as the Ba salt (Raney Ni in H_2O) at 125°/3000 lb. to 3:4:5-trimethyl-*l*-galacturonic acid, m.p. 161—162°, $[\alpha]_{\text{D}}^{25} +12.6^\circ$ in H_2O . The rate of hydrolysis of 2:3:4-trimethyl- α -methyl-*d*-galactoside *Me* ester ($[\alpha]_{\text{D}}^{25} +199.1^\circ \rightarrow +109.7^\circ$ in 2.5 hr. in N-HCl at 100°) is similar to that of (I) ($[\alpha]_{\text{D}}^{25} +166.2^\circ \rightarrow +104.1^\circ$ in 3 hr.). R. S. C.

α -Phenylsulphonylpropionic acid. L. RAMBERG and I. HEDLUND (Arkiv Kemi, Min., Geol., 1938, 12, A, No. 24, 12 pp.).—*dl*-SPh-CHMe-CO₂Na and KMnO_4 give *dl*-PhSO₂-CHMe-CO₂H (I), m.p. 115.1—115.6° (amide, m.p. 150.2—150.5°; dimethylamide, m.p. 82.1—82.4°). The effect of various acids, salts, and org. substances on the solubility of (I) in H_2O is detailed. *d*-SPh-CHMe-CO₂Na, $[\alpha]_{\text{D}}^{25} +46.5^\circ$, and KMnO_4 in the presence of CO_2 and the theoretical amount of H_2SO_4 give *d*- α -phenylsulphonylpropionic acid, m.p. 72.5—73.5°, $[\alpha]_{\text{D}}^{25} +48^\circ$, $+51.4^\circ$, $[\alpha]_{\text{D}}^{25} +57.2^\circ$, $+61.9^\circ$ in H_2O and 0.1N-HCl, respectively (dimethylamide, m.p. 96.8—97.3°, $[\alpha]_{\text{D}}^{25} +38.4^\circ$ in H_2O). M.p. are corr. R. S. C.

Formaldehyde formation in the photo-oxidation of organic compounds and the formaldehyde theory of carbon assimilation. A. RAM and N. R. DHAR (J. Indian Chem. Soc., 1938, 15, 321—345).—On the basis of the amounts of CH_2O formed during photo-oxidation in dil. solution, the org. substances investigated have been divided into three groups. (a) Where CH_2O is formed as a direct product of photo-oxidation (e.g., AcOH, citric, malic, and lactic acids, and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, dyes, glycerol, guaiacol etc.). (b) CH_2O formed partly by direct photo-oxidation and partly by photosynthesis from CO_2 generated during oxidation (tartaric, propionic, butyric acid, etc.). (c) CH_2O formed by photosynthesis from active CO_2 produced by photo-oxidation (sugars, dibasic acids, NH_2 -acids, and Na salts and esters of fatty acids). Formation of CH_2O is not limited to substances of biochemical origin, but can be detected in any substance which can be photo-oxidised to CO_2 and H_2O ; the formation of CH_2O is easier from substances oxidising to CO_2 than from CO_2 solutions as in the former case the CO_2 is liberated in an active condition. In phyto-synthesis, the energy of respiration of the plant is assumed to supply some of the energy required for the synthesis of CH_2O from CO_2 , although light, moisture, and chlorophyll are also necessary.

J. D. R.

Crotonaldehyde condensations. H. L. DU MONT and H. FLEISCHHAUER (Ber., 1938, 71, [B], 1958—1962).—Condensation of $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ with piperidine acetate at room temp. affords *o*-dihydrotolualdehyde, octatrienal, and dodecapentaenal; the total yield of condensation products is ~25% and the individual yields are too variable to permit theoretical conclusions. Admixture of $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ with varying amounts of catalyst and measurement of the time necessary for the production of striae at room temp. shows that up to a concn. of about 1% the rate of condensation \propto the concn. of catalyst. Similar measurements in the presence of MeOH, EtOH, Pr^nOH , Pr^iOH , Bu^nOH , Bu^iOH , and isoamyl alcohol show a very marked influence of the constitution of the solvent (40 min. required in Pr^nOH and only 2 min. in Pr^iOH). $\text{C}_6\text{H}_5\text{N}$ behaves like an alcohol but AcOH is remarkably restrictive. Solvents without reactive groups (Et_2O , dioxan, C_6H_6 , CHCl_3 , and EtOAc) become only faintly coloured and do not speedily yield a ppt.

H. W.

Methyl ethyl ketone. S. L. LANGEDIJK (Chem. and Ind., 1938, 891—898).—Preps., physical and chemical properties, solvent power, and uses of this substance are given.

K. W. P.

Cleavage of the carbon chain of glucosides by oxidation with lead tetra-acetate. W. S. McCLENAHAN with R. C. HOCKETT (J. Amer. Chem. Soc., 1938, 60, 2061—2063).— $\text{Pb}(\text{OAc})_4$ (modified prep.) in AcOH or, better, CHCl_3 cleaves the C chain of methylpyranosides to give products, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{CHO})\cdot\text{O}\cdot\text{CH}(\text{OMe})\cdot\text{CH}(\text{OH})\cdot\text{CHO}$ or $\text{CHO}\cdot\text{CH}(\text{OMe})\cdot\text{O}\cdot\text{CH}(\text{CHO})\cdot\text{CH}_2\cdot\text{OH}$, which are not isolated as they react further to give $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{CHO})\cdot\text{O}\cdot\text{CH}(\text{OMe})\cdot\text{CHO}$. Treatment with $\text{Br}\cdot\text{SrCO}_3$ then gives the same products as are

obtained by HIO_4 . Examples are α -methyl-*d*-mannoside and -*d*-glucoside, and β -methyl-*d*-arabinoside: α -Methyl-*d*-lyxoside gives an acid, $[\alpha]_D^{20} -11.5^\circ$ in H_2O (Sr salt, $[\alpha]_D^{20} -56.6^\circ$ in H_2O). R. S. C.

Cleavage of the carbon chain of α -methyl-*d*-lyxopyranoside by oxidation with periodic acid. W. D. MACLAY and C. S. HUDSON (J. Amer. Chem. Soc., 1938, 60, 2059—2060).—The ring-structure of α -methyl-*d*-lyxoside is proved by oxidation by 2 mols. of HIO_4 to $\text{CHO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}(\text{OMe})\cdot\text{CHO}$, which with $\text{Br}\cdot\text{SrCO}_3$ gives Sr *D*'-methoxydiglycollate, identical with that obtained from α -methyl-xylo- and -arabinopyranoside. R. S. C.

Glucofuranosides and thioglucofuranosides. III. Crystalline furanosides of *d*-galactose and *l*-arabinose. J. W. GREEN and E. PACSU (J. Amer. Chem. Soc., 1938, 60, 2056—2057; cf. A., 1938, II, 44).— β -Methyl-, m.p. 63—65°, $[\alpha]_D^{20} -108^\circ$, β -propyl-, m.p. 89—90°, $[\alpha]_D^{20} -100^\circ$, and β -benzyl-galactofuranoside, m.p. 80—81°, $[\alpha]_D^{20} -96^\circ$, α -methyl-, $[\alpha]_D^{20} -125^\circ$, and α -ethyl-*l*-arabinofuranoside, m.p. 48—49°, $[\alpha]_D^{20} -116^\circ$, are prepared by shaking the Et mercaptal of galactose or arabinose with HgCl_2 , HgO , and anhyd. CaSO_4 in the appropriate abs. alcohol. $[\alpha]$, which are in H_2O , agree with Hudson's isorotation rules. R. S. C.

Presence of anhydro-*l*-galactose in agar-agar. S. HANDS and S. PEAT (Chem. and Ind., 1938, 937—938).—Agar-agar is directly methylated by $\text{Me}_2\text{SO}_4\text{-NaOH}$ to a product (OMe'' 33.0%; $[\alpha]_D^{16} -93.1^\circ$ in CHCl_3 ; S absent), hydrolysis of which by boiling 2% $\text{HCl}\text{-MeOH}$ gives α - and β -methyl-2:4:6-trimethyl-*d*-galactopyranoside, α -methyl-2:4-dimethyl-3:6-anhydro-*l*-galactopyranoside (I), m.p. 82—83°, $[\alpha]_D +85.3^\circ$ in CHCl_3 , $+73^\circ$ in H_2O , $+77.8^\circ \rightarrow -21^\circ$ in dil. H_2SO_4 , and a trace of an ester (removed as Ba salt), but no tetramethylgalactose or dimethylketose derivative. The structure of (I) follows from its stability to hot $\text{NaOMe}\text{-MeOH}$ and hydrolysis by cold acid to 2:4-dimethyl-3:6-anhydro- α -*l*-galactose (II), m.p. 114°, from the properties of the synthetic *d*-forms of (I) (m.p. 82—83°, $[\alpha]_D -86.6^\circ$ in CHCl_3 , -76° in H_2O , $-69.4^\circ \rightarrow +20^\circ$ in dil. H_2SO_4) and (II) (m.p. 115°) (syntheses unpublished), and from the identical X-ray spectra of both forms of (I). Hydrolysis of methylated hexose-polysaccharides by conc. mineral acid leads to partial decomp. to lævulic acid. R. S. C.

Preparation of higher alkylglucosides. C. R. NOLLER and W. C. ROCKWELL (J. Amer. Chem. Soc., 1938, 60, 2076—2077).—Acetobromoglucose, Ag_2O , and the appropriate aldehyde in Et_2O give 40—60% of *n*-hexyl-, m.p. 51—52.5°, $[\alpha]_D^{25} -22.4^\circ$, *n*-octyl-, m.p. 53—54°, $[\alpha]_D^{25} -21.7^\circ$, *n*-nonyl-, m.p. 39.5—40.5°, $[\alpha]_D^{25} -20.9^\circ$, *n*-decyl-, m.p. 47.5—48.5°, $[\alpha]_D^{25} -21.5^\circ$, and *n*-dodecyl-glucoside tetra-acetate, m.p. 58.5—59.5°, $[\alpha]_D^{25} -18.8^\circ$, converted by NaOMe into the free glucosides, m.p. 88—91°, 65—99°, 65—118°, 75—130°, and 77—137°, $[\alpha]_D^{25} -33.7^\circ$, -30.3° , -28.8° , -27.8° , and -24.7° , respectively. $[\alpha]$ are in MeOH. The lower figure of the m.p. of the glucosides represents liquid crystal formation, the higher final melting.

R. S. C.

Syntheses with 5:6-anhydroisopropylidene-glucose. VI. Glucose 6-alkyl ethers. H. OHLE and K. TESSMAR (Ber., 1938, 71, [B], 1843—1854; cf. A., 1938, ii, 83).—The experiments were undertaken to explain the abnormalities arising in the application of the "CPh₃ method" (Helferich and Becker, A., 1924, i, 9; Ohle and von Vargha, A., 1929, 1279; Helferich and Günther, A., 1931, 939). 6-Triphenylmethyl-1:2-isopropylideneglucose 3:5-dibenzoate is transformed by HCl in abs. CHCl₃ into non-cryst. 1:2-isopropylideneglucose 3:5-dibenzoate and 1:2-isopropylideneglucose 3:6-dibenzoate from which 1:2-isopropylideneglucose 3:6-dibenzoate 5-*p*-toluenesulphonate (I) is isolated by the action of *p*-C₆H₄Me-SO₂Cl. Under the influence of HCl a migration of Bz from C₍₅₎ to C₍₆₎ has occurred. If the syrupy mixture is treated with Ag₂O in boiling C₆H₆ and treated after some time with *p*-C₆H₄Me-SO₂Cl the product is (I) and 1:2-isopropylideneglucose 5:6-dibenzoate 3-*p*-toluenesulphonate; under the influence of Ag₂O, Bz has wandered from C₍₃₎ to C₍₆₎. Re-esterification in an acid medium and acyl migration in an alkaline medium have therefore a different reaction mechanism and in esterified polyhydric alcohols may be operative at different ester groups. Under the same conditions migration of Bz is not observed with α -methylglucoside 2:3:4-tribenzoate. Benzoylation of 6-methylglucose in C₅H₅N gives 6-methylglucose 1:2:3:4-tetrazobenzoate, which is transformed by HBr-AcOH into non-cryst. 1-bromo-6-methylglucose 2:3:4-tribenzoate; this with abs. MeOH and Ag₂O yields the cryst. 6-methyl- β -methylglucoside 2:3:4-tribenzoate, converted by TiCl₄ in CHCl₃ into 6-methyl- α -methylglucoside 2:3:4-tribenzoate. The discrepant behaviour of the 6-methylglucose of Helferich (*loc. cit.*) cannot therefore be due to the presence of other methylglucoses. The 6-methyl- α -methylglucoside tribenzoate (II), m.p. 116—117°, is however, not homogeneous but contains about 10% of α -methylglucoside 2:3:4-tribenzoate, which is separated after hydrolysis (Zemplén) as α -methylglucoside; also the OMe is very sensitive to acid and readily removed. This is particularly obvious during the action of HBr-AcOH on 6-methoxyglucose 1:2:3:4-tetrazobenzoate; if reaction is prolonged to 20 hr. smooth acetolysis to 1-bromoglucose 2:3:4-tribenzoate 6-acetate (converted into β -methylglucoside 2:3:4-tribenzoate 6-acetate in 70% yield) is observed. Methylation of (II) and hydrolysis (Zemplén) of the product gives amorphous 6-methyl- α -methylglucoside, transformed by 10% HCl at 60° into homogeneous 6-methylglucose in yield < that obtained by use of the isopropylidene compound. The following 6-alkylisopropylideneglucoses are obtained by the action of a solution of Na in the requisite alcohol on isopropylideneglucose at room temp. (C₅H₅N as catalyst appears more liable to induce polymerisation): *-ethyl-*, b.p. 150—160°/0.15 mm., m.p. 56—58°, [α]_D²⁰ +4.8° in CHCl₃; *-n-propyl-*, b.p. 170—180°/0.15 mm., [α]_D²⁰ -7.3° in CHCl₃; *-isopropyl-*, b.p. 162—170°/0.10 mm., m.p. 65.6—67°, [α]_D²⁰ +6.6° in CHCl₃; *-benzyl-*, b.p. 220—240°/0.15 mm., m.p. 78.5—79°, [α]_D²⁰ +2.0° in CHCl₃. Hydrolysis of these with boiling 50% AcOH gives the 6-alkyl-glucoses; *-ethyl-*, m.p. 161—165°, [α]_D²⁰ +84.8° to +51.1° in H₂O; *-n-propyl-*, o* (A., II).

m.p. 118—120°, [α]_D²⁰ +84.2° to +48.9° in H₂O; *-isopropyl-*, m.p. 123—125°, [α]_D²⁰ +80.3° to +49.4° in H₂O; *-benzyl-*, m.p. 92—93.5°, [α]_D²⁰ +70.2° to +39.3° in H₂O. H. W.

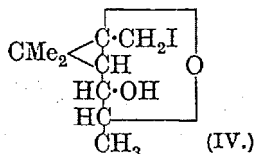
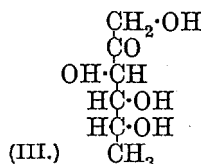
The anhydromethylhexoside formed by alkaline hydrolysis of 2-*p*-toluenesulphonyltriacyl- β -methylglucoside. Characterisation of 2:4:6-trimethylglucose. W. H. G. LAKE and S. PEAT (J.C.S., 1938, 1417—1421; cf. A., 1938, II, 348).—The dimethylanhydromethylhexoside, m.p. 69°, described by Haworth *et al.* (A., 1934, 394) is dimethyl-2:3-anhydro- β -methylmannopyranoside; when refluxed with NaOMe-MeOH for 24 hr., it yields an equimol. mixture of 2:4:6-trimethyl- β -methyl-*d*-glucopyranoside (I), m.p. 71°, [α]_D²² -27.0° in CHCl₃ (cf. Oldham, A., 1934, 872), and 3:4:6-trimethyl- β -methyl-*d*-altropyranoside (II), [α]_D²¹ -25.6° in CHCl₃, suggesting cleavage of the C₍₂₎-C₍₃₎ anhydro-ring with equal facility on either side of O (mechanism discussed). (I) (Purdie reagents) affords tetramethyl- β -methylglucopyranoside, m.p. 38—39°, [α]_D²⁰ -17.1° in H₂O, hydrolysed by 7% HCl for 4 hr. at 100° to tetramethyl- α -*d*-glucopyranose, m.p. 87°, [α]_D²⁰ +93.0° \rightarrow +84.0° (equilibrium val.) in H₂O. (I) and 7% HCl for 3 hr. give 2:4:6-trimethyl- α -glucopyranose, m.p. 115°, [α]_D²⁰ +98.2° \rightarrow +74.8° (equilibrium val.) in H₂O, converted by aq. Br at room temp. into 2:4:6-trimethyl-8-gluconolactone, b.p. 140°/0.01 mm., [α]_D²¹ +96° \rightarrow +39.0° (const.) in 6 hr. in H₂O (trimethylhexonic acid, [α]_D²¹ +37.5° \rightarrow +40.0° in 3 hr.). The lactone and liquid NH₃ afford an α -methoxyamide, m.p. 100°, [α]_D²⁰ +37.0° in CHCl₃. (II) similarly gives tetramethyl- β -methylaltropyranoside, b.p. 86°/0.006 mm., [α]_D¹⁷ -38.0° in CHCl₃, converted by 7% HCl into tetramethyl-*d*-altropyranose, [α]_D¹⁹ +63.0° in CHCl₃. Oxidation with HNO₃ (*d* 1.42) then gives *d*-arabotrimethoxyglutaric acid and *l*-dimethoxysuccinic acid, and a trace of *i*-xylotrimethoxyglutaric acid; the constitutions of the acids are shown by conversions through the Me esters into the methylamides, m.p. 172°, 206°, and 167°, and [α]_D²⁰ -60.3°, -131.0°, and 0.0° in H₂O, respectively. (II) and 7% HCl give 3:4:6-trimethylaltrose, [α]_D²⁰ +53.0° in H₂O (with a little trimethylglucose), oxidised by Br-H₂O to 3:4:6-trimethyl-8-altrolactone, b.p. 150°/0.02 mm., [α]_D¹⁹ -9.6° \rightarrow +10.8° (const.) in 24 hr. in H₂O. It yields an α -OH-amide. The views of Peat and Wiggins (*loc. cit.*) on the alkaline hydrolysis of a sugar *p*-toluenesulphonate are corroborated. A. T. P.

Osazones; *d*- and *l*-dianhydrohexosazone. E. G. V. PERCIVAL (J.C.S., 1938, 1384—1386; cf. A., 1938, II, 309).—The formulæ accorded to glucosazone (A., 1935, 1484) and dianhydrohexosazone (I) from *d*-glucosazone and *d*-galactosazone (A., 1937, II, 51) are supported. (I) and *p*-C₆H₄Me-SO₂Cl in C₅H₅N for 40 hr. afford the *p*-toluenesulphonate, m.p. 205—206°, [α]_D²⁰ +38° in COMe₂, unchanged by NaI-COMe₂ at 100° for 25—100 hr. Thus $\cdot\text{CH}_2\cdot\text{OH}$ is absent in (I). *d*-Gulonolactone and Na-Hg give a crude glucose, [α]_D¹⁴ -17° in H₂O, converted by NHPH-NH₂, HCl-NaOAc-NaHSO₃ at 95—100° for 3 hr. into *d*-gulosazone. This and Ac₂O-C₅H₅N at room temp. yield *d*-gulosephenylosazone tetra-acetate,

m.p. 75—85°, $[\alpha]_D^{25} + 70^\circ$ in CHCl_3 , deacetylated in $\text{NaOH}-\text{COMe}_2-\text{H}_2\text{O}$ to (I). Anhydride formation is thus concerned with OH on $\text{C}_{(3)}$ and $\text{C}_{(4)}$. A Walden inversion can occur on either $\text{C}_{(3)}$ or $\text{C}_{(4)}$ or both, to give the most stable arrangement of the three rings (formulae given). 1-Sorboseazone tetra-acetate, m.p. 75—85°, $[\alpha]_D^{25} - 70^\circ$ in CHCl_3 , gives the corresponding 1-enantiomorph of (I), m.p. 237°, $[\alpha]_D^{25} + 89^\circ$ in COMe_2 (Ac derivative, m.p. 135°, $[\alpha]_D^{25} - 107^\circ$ in CHCl_3).

A. T. P.

2-Ketomethylpentoses. III. d-Fructomethyl-ose. W. T. J. MORGAN and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 1023—1031; cf. A., 1938, II, 172).—Fructose with >2 mols. of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ affords considerable amounts of non-cryst. d-fructose 1:6-di-p-toluenesulphonate since treatment of the product with $\text{COMe}_2-\text{CuSO}_4-\text{H}_2\text{SO}_4$ at room temp. leads to 2:3-isopropylidene-d-fructofuranose 1:6-di-p-toluenesulphonate (I), m.p. 132—133° (corr.), $[\alpha]_D^{20} + 14.5^\circ \pm 0.8^\circ$ in abs. EtOH, also obtained directly from 2:3-isopropylidene-d-fructofuranose, into which it is re-transformed by 4% Na-Hg in 80% MeOH at room temp. (I) with NaI in COMe_2 at 100° yields 6-iodo-2:3-isopropylidene-d-fructomethyl-ose 1-p-toluenesulphonate, m.p. 124—125°, $[\alpha]_D^{20} + 7.5^\circ \pm 0.5^\circ$ in abs. EtOH, hydrogenated (Raney Ni-MeOH) to 2:3-isopropylidene-fructomethyl-ose 1-p-toluenesulphonate (II), m.p. 113—114°, $[\alpha]_D^{21} + 11.0^\circ \pm 2^\circ$ in abs. EtOH. This is converted by Na-Hg in 80% MeOH into 2:3-isopropylidene-d-fructomethyl-ose, m.p. 114—115° (corr.), $[\alpha]_D^{20} + 8.3^\circ \pm 0.5^\circ$ in abs. EtOH, hydrolysed (10% AcOH at 100°) to d-fructomethyl-ose (III), $[\alpha]_D^{22} - 6.0^\circ \pm 0.5^\circ$ in H_2O (o-nitrophenylhydrazine, m.p. 136—137° (corr.), $[\alpha]_D^{20} + 40^\circ \pm 3^\circ$ in abs. EtOH), which could not be obtained cryst. and readily reduces Fehling's solution. With NaI in COMe_2 at 125° (II) yields 1-iodo-2:3-isopropylidene-1-deoxy-d-fructomethyl-ose (IV), m.p. 102—103° (corr.), $[\alpha]_D^{22} - 35^\circ \pm 2^\circ$ in abs. EtOH, dehalogenated (Raney Ni) to 2:3-isopropylidene-1-deoxy-d-fructomethyl-ose, m.p. 62—64°, $[\alpha]_D^{22} + 6.6^\circ \pm 0.5^\circ$ in abs. EtOH.



propylidene-d-fructomethyl-ose, m.p. 114—115° (corr.), $[\alpha]_D^{20} + 8.3^\circ \pm 0.5^\circ$ in abs. EtOH, hydrolysed (10% AcOH at 100°) to d-fructomethyl-ose (III), $[\alpha]_D^{22} - 6.0^\circ \pm 0.5^\circ$ in H_2O (o-nitrophenylhydrazine, m.p. 136—137° (corr.), $[\alpha]_D^{20} + 40^\circ \pm 3^\circ$ in abs. EtOH), which could not be obtained cryst. and readily reduces Fehling's solution. With NaI in COMe_2 at 125° (II) yields 1-iodo-2:3-isopropylidene-1-deoxy-d-fructomethyl-ose (IV), m.p. 102—103° (corr.), $[\alpha]_D^{22} - 35^\circ \pm 2^\circ$ in abs. EtOH, dehalogenated (Raney Ni) to 2:3-isopropylidene-1-deoxy-d-fructomethyl-ose, m.p. 62—64°, $[\alpha]_D^{22} + 6.6^\circ \pm 0.5^\circ$ in abs. EtOH.

H. W.

Crystallised l-tagatomethyl-ose. J. BARNETT and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 913—914; cf. A., 1938, II, 5).—l-Tagatomethyl-ose has been obtained cryst.; it has m.p. 68—69°, $[\alpha]_D^{22} + 3^\circ \pm 1^\circ$ in H_2O .

H. W.

Crystalline dimethyl acetal of d-fructose. E. PACSU (J. Amer. Chem. Soc., 1938, 60, 2277—2278).—Fructose Et_2 mercaptal, HgCl_2 , and HgO in abs. MeOH at -80° give abnormally d-fructose Me_2 acetal, m.p. 107—108°, $[\alpha]_D^{20} - 45.6^\circ$ in H_2O (penta-acetate, m.p. 109°, $[\alpha]_D^{20} 0^\circ$ in CHCl_3), fermented by yeast in distilled H_2O , but not in a citric acid- Na_2HPO_4 buffer at p_H 7, and unaffected by invertase at p_H 4.5 or 7. The acetal is stable in alkaline or

neutral solution, but is rapidly decomposed by acid. It does not reduce Fehling's solution. R. S. C.

Vegetable heart poisons. XVII. Subsidiary glucosides of the oleander. R. TSCHESCHE, K. BOHLE, and W. NEUMANN (Ber., 1938, 71, [B], 1927—1932; cf. A., 1938, II, 174).—Hydrogenation (PtO_2) of tetrahydroanhydroadynenigenin (I) in AcOH containing conc. HCl at 70—80° gives the saturated lactone, $\text{C}_{23}\text{H}_{33}\text{O}_2$, m.p. 187—188°, from digitoxigenin, showing that the C skeleton of adynenigenin (II) is identical with that of the other heart poison aglucones and that the steric relationships at $\text{C}_{(17)}$ correspond with those of the physiologically active glucosides. Similar hydrogenation of the acetate of (I) followed by hydrolysis and oxidation with CrO_3 leads to tetrahydroanhydrodigitoxigenone. The sec.-OH of (II) must therefore be at $\text{C}_{(3)}$ and sterically in the same position as in digitoxigenin since neither genin is pptd. by digitonin. The isolation of neriantin (III) from the oleander glucosides is described; its presence is not universal and the possibility that it is a transformation product is not excluded. It is $\text{C}_{29}\text{H}_{42}\text{O}_9 \cdot 1.5\text{H}_2\text{O}$, m.p. 206—208°, $[\alpha] \pm 0^\circ$. H_2O of crystallisation is very tenaciously retained. (III) has no cardiac action. It absorbs 2 H_2 when hydrogenated. When hydrolysed (III) affords glucose and neriantogenin (IV), $\text{C}_{23}\text{H}_{32}\text{O}_4$, m.p. 255—259°. Conc. HCl at room temp. transforms (IV) into dianhydrodigitoxigenin, establishing the C skeleton of (IV) and proving the presence of OH at $\text{C}_{(3)}$. The OH removed by conc. HCl is probably sec. since (IV) readily gives a di-acetate, m.p. 184—185°, which differs from Δ^{14} -anhydro-oleandrigenin acetate, m.p. 168—170°.

Hydrolysis of oleandrin or adynenigenin with 10% HCl-MeOH at room temp. and oxidation of the syrupy oleandrose (V) with Br in presence of $\text{Ba}(\text{OBz})_2$ gives oleandronic acid, the phenylhydrazide, m.p. 136°, $[\alpha]_D + 20.3^\circ$ in MeOH, of which is not identical with cymarophenylhydrazide. Cymarose and (V) are therefore not identical. (V) is methylated and transformed into methyl-oleandronic acid, characterised as the phenylhydrazide, m.p. 94°, $[\alpha]_D - 7.1^\circ$ in CHCl_3 , not identical with the phenylhydrazide of 4- or 5-methylcymaronic acid.

H. W.

Trillarin, $\text{C}_{37}\text{H}_{59}\text{O}_{14}$, m.p. 211°, and trillari-genin, $\text{C}_{25}\text{H}_{39}\text{O}_4$, m.p. 197°.—See A., 1938, III, 837.

Glucoside, $\text{C}_{22}\text{H}_{24}\text{O}_{11}$, from Lotus arabicus.—See A., 1938, III, 859.

So-called "amylobiose." K. MYRBÄCK and B. ÖRTENBLAD (Svensk Kem. Tidskr., 1938, 50, 185—189).—The products obtained by Pringsheim (A., 1926, 715) by the action of cold, conc. HCl on starch were not homogeneous under any conditions and were mainly composed of materials of much higher mol. wt. than a di- or tri-saccharide. The existence of amylo-biose or -triose is not established and is improbable. It is not denied that the products of the degradation of starch by cold, conc. HCl differ in some properties, i.e., $[\alpha]_D$, from those obtained with the hot dil. acid.

H. W.

Galactogen from the albumin glands of Helix pomatia. E. BALDWIN and D. J. BELL (J.C.S.,

1938, 1461—1465; cf. May, A., 1934, 914, 1251; Schlubach and Loop, A., 1937, II, 486).—Dried albumin glands of *H. pomatia* and 30% NaOH at 100° for 3 hr., then 30% KOH at 100° for 2 hr., afford galactogen (I), $[\alpha]_D^{20} +16.1^\circ$ in H_2O , containing 0.2% of org. P, and hydrolysed to *d*-galactose. (I) and $C_5H_5N \cdot Ac_2O$ at room temp. for 12 hr. and then at 70° for 4 hr. give a triacetate, which with Me_2SO_4 —KOH— $COMe_2$ at 100° yields a residue having 25.6% OMe; 13 such methylations raise the OMe val. to 43.1%, $[\alpha]_D^{20} -20^\circ$ in H_2O . This methylated (I) in conc. HCl is saturated with HCl at -15° , and after 2 hr. affords 2:3:4:6-tetramethyl- and 2:4-dimethyl- (II) (hydrate, m.p. 98°, $[\alpha]_D^{20}$ at equilibrium $+85.7^\circ$ in H_2O ; 4-methyl-*d*-galactosazone, m.p. 148—150°) *d*-galactopyranose. (II), through the corresponding acid, gives a δ -galactonolactone (vals. of $[\alpha]$), converted into 2:4-dimethyl-*d*-galactonamide. There is no evidence of sugars other than *d*-galactose in (I).

The structure of (I) (formulae suggested) is of a new type and may be a chain of *d*-galactopyranose (III) units linked 1:3 (or 1:6) (probably in β -configuration), each unit bearing as side-chain a single (III) unit, glycosidically linked at C_6 (or C_3). An alternative is a closed loop of (III) units.

A. T. P.

Determination of terminal groups in cellulose and starch. K. HESS (Papier-Fabr., 1938, 36, 333—339).—An account is given of the method of Hess and Neumann (A., 1937, II, 232) for the separation of 2:3:4:6-tetramethylmethylglucoside from much larger amounts of 2:3:6-trimethylmethylglucoside, and its application to the determination of the mol. chain-lengths of cellulose and starch. Trimethylcellulose (41.9—42.2% OMe), prepared in absence of air from suitably purified cellulose, yields no tetramethylglucose on hydrolysis. Trimethylstarch yields approx. 1.9%. On the mol. chain hypothesis the cellulose mol. is either a ring or very long, and that of starch consists of 52 glucose units. Since preps. of starch of apparently identical chain-length differ in η it is concluded that they differ in their respective states of aggregation.

W. A. R.

Polysaccharides. XXVIII. The "end-group" method as applied to starch. Improved method for estimating tetramethylglucose in admixture with trimethylglucose. E. L. HIRST and G. T. YOUNG (J.C.S., 1938, 1247—1252; cf. following abstract).—The "end-group" method of Haworth and Machemer as employed by Hirst *et al.* (A., 1932, 1116) is accurate (cf. Hess and Lung, A., 1938, II, 221); that of Hess and Neumann (*loc. cit.*) is unreliable. A modification is suggested whereby the applicability of the "end-group" method in chain-length determinations is widened and results are rendered more accurate. Tetramethylmethylglucoside can be estimated accurately by fractional distillation of the mixed glucosides. When these have not been allowed to reach equilibrium with respect to their α - and β -forms, excess of the latter leads to high vals. for tetramethylglucose (I). This is overcome by measuring $[\alpha]_D$ (in H_2O) and η^{16} during fractional distillation and comparing the vals. with those

obtained from synthetic mixtures of the corresponding α - and β -methylglucosides, whereby the points at which pure tetra- ceases, and at which pure trimethylmethylglucoside begins, to distil, can be detected. Conditions of glucoside formation should ensure absence of furfuraldehyde, which otherwise can be removed by cold 0.04*N*- $KMnO_4$. Traces of Me lavulate can be separated by careful fractional distillation.

A. T. P.

Polysaccharides. XXVII. The "end-group" method as applied to cellulose. F. J. AVERILL and S. PEAT (J.C.S., 1938, 1244—1247).—The "end-group" method for determination of mol. size of polysaccharides (Haworth and Machemer, A., 1932, 1022) is applicable even to lower concns. of tetramethylglucose (1 pt. in 1000 pts. of trimethylglucose detected) than are obtained usually in the hydrolysates of methylated cellulose, and the criticism of Hess and Neumann (A., 1937, II, 232) has no foundation. The claim of Neumann and Hess (*loc. cit.*) to separate tetra- from tri-methylmethylglucoside by an alternative method is not substantiated.

A. T. P.

Highly polymerised compounds. CXCV. Solutions of cellulose xanthate. H. STAUDINGER and G. DAUMILLER (Ber., 1938, 71, [B], 1995—2002).—Linters, bleached in differing degrees, is treated with 18% NaOH for 2 hr. at room temp., after which part of the alkali is removed. The residue is shaken for 16 hr. at 3—5° or for 8—10 hr. at 18—20° with CS_2 , giving products xanthated in differing degree. These are washed with MeOH (better EtOH) and Et_2O , dried for 24 hr. at 15°/high vac., and the viscosity of their solution in 8% NaOH is determined under N_2 at 20°. The esters are cautiously hydrolysed by H_2SO_4 and the viscosity of the regenerated celluloses is determined in Schweitzer's reagent. In every case the ratio of the η_{sp}/c vals. of the xanthate to that of the cellulose solution is approx. const. although the products vary greatly in degree of polymerisation. The colloid particles of the xanthate solutions have therefore the same structure as the cellulose particles in Schweitzer's solution and the conversions of xanthates into celluloses are polymeric-analogous transformations. The xanthates are macromols., not micelles. The viscosity of the xanthates depends very greatly on the degree of esterification, highly xanthated products giving less viscous solutions than polymeric-analogously less highly xanthated specimens. The increase of the viscosity of xanthate solutions during after-ripening is due to removal of xanthate groups by hydrolysis and not to an increase in mol. size.

H. W.

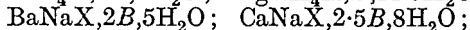
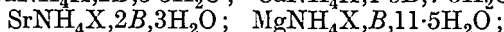
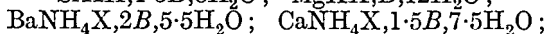
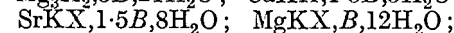
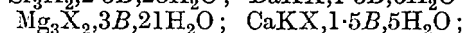
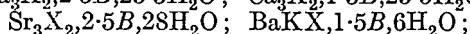
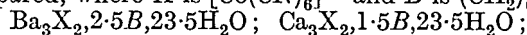
Catalytic dehydration. S. CHATTERJEE, M. SAN-YAL, and M. GOSWAMI (J. Indian Chem. Soc., 1938, 15, 399—401).— Et_2O , Pr^a_2O , Bu^a_2O , or $(n-C_5H_{11})_2O$ with NH_3 in presence of ThO_2 or Al_2O_3 at 200—425° gives 0.3502—8.262% of *sec.* base. However, Et_2O and NH_2Ph in presence of Al_2O_3 , best at 370—400°, give 71—74% of $NPhEt_2$ and 14—17% of $NHPhEt$.

R. S. C.

Cyclic methyleneamines. Hydrolysis of quaternary compounds. Preparation of aliphatic secondary amines. I. J. GRAYMORE (J.C.S., 1938,

1311—1313).— $\text{NEt} \begin{array}{c} \text{CH}_2 - \text{NEt} \\ \text{CH}_2 \cdot \text{NEt}_2 \text{I} \end{array} \text{CH}_2$ (I), m.p. 95—100° (decomp.), and H_2O form the hydriodide, m.p. 124°, and CH_2O (II), but evaporation with aq. HCl affords much (II) and salts of NHEt_2 and NH_2Et . Mechanisms of hydrolysis are suggested. The methiodide, new m.p. 98—100°, corresponding with (I), and excess of H_2O , then excess of KOH , give $(\text{CH}_2)_6\text{NEt}_3$, NHMeEt , EtCN (?), and *s*-dimethyldiethylmethylenediamine, $\text{CH}_2(\text{NMeEt})_2$ (III), b.p. 131° [gives (II) slowly in moist air]. (III) and conc. HCl on evaporation to a syrup give much (II); addition of H_2O — NaNO_2 then yields $\text{NMeEt}\cdot\text{NO}$, b.p. 163°/747 mm., converted by refluxing with conc. HCl for 5 hr., into NHMeEt , b.p. 35—38° (hydrochloride, m.p. 124—125°; 2 : 4- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NMeEt}$, m.p. 55°), which with *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}\cdot\text{NaOH}$ gives an oil, b.p. 210°/50 mm. A. T. P.

Compounds of hexamethylenetetramine with simple and double salts of cobalticyanic acid and the nature of residual affinity. B. K. GHOSH (J. Indian Chem. Soc., 1938, 15, 305—310).—By interaction of the appropriate metal cobalticyanide and $(\text{CH}_2)_6\text{N}_4$ in H_2O the following compounds are prepared, where X is $[\text{Co}(\text{CN})_6]^{4-}$ and B is $(\text{CH}_2)_6\text{N}_4$:



$\text{SrNaX}\cdot 2\text{B}\cdot 7.5\text{H}_2\text{O}; \text{MgNaX}\cdot 1.5\text{B}\cdot 13\text{H}_2\text{O}$. Comparison of the above formulæ with those of the cobalticyanides themselves shows that association with $(\text{CH}_2)_6\text{N}_4$ increases the capacity of the simple cobalticyanides for union with H_2O , but decreases that of the double cobalticyanides. These anomalies are considered to be due to alterations in the electric field around the complex ion. J. D. R.

Photochemical deamination of amino-acids in water.—See A., 1938, I, 528.

Enzymic degradation and synthesis of glutamic acid.—See A., 1938, III, 950.

Rate of reaction of thiol and disulphide compounds with phosphotungstic acid and with sulphite. (Miss) B. KASSELL and E. BRAND (J. Biol. Chem., 1938, 125, 131—144).—Many SH- and S-S-compounds are shown photometrically to react more slowly with phospho-18-tungstic acid with and without Na_2SO_3 than do cystine and cysteine, but the rate of reaction is increased if these two substances are also present. R. S. C.

N-Methylcysteine and derivatives. K. BLOCH and H. T. CLARKE (J. Biol. Chem., 1938, 125, 275—287).—*S*-Benzylcysteine (I) and HCl in BuOH give the *Bu* ester hydrochloride, m.p. 131°, the free ester from which with $\text{MeI}\cdot\text{C}_6\text{H}_5$ gives a product, hydrolysed by HCl to impure *S*-benzyl-N-methylcysteine. The PhSO_2 derivative, m.p. 137°, of (I) with $\text{Me}_2\text{SO}_4\cdot 2\text{N}\cdot\text{NaOH}$ gives a gum. Di-*p*-toluenesulphonylcysteine, m.p. 213—215° (lit. 201—203°), and $\text{Me}_2\text{SO}_4\cdot 2\text{N}\cdot\text{NaOH}$ give di-*p*-toluenesulphonyldi-N-methylcysteine,

m.p. 125—127°, $[\alpha]_D^{24} + 57.7^\circ$ in *n*- NaOH , converted by Na in liquid NH_3 into N-methylcysteine [hydrochloride (II), m.p. 128—130° (decomp.; softens at 100°), $[\alpha]_D^{23} + 9.21^\circ$ in H_2O ; *Ac* derivative, m.p. 132°, $[\alpha]_D^{24} - 44.5^\circ$ in H_2O], which with FeSO_4 yields NN'-dimethylcysteine (III), m.p. 217° (decomp.), $[\alpha]_D^{24} - 117.8^\circ$ in H_2O , $+ 92.3^\circ$ in *n*- NaOH , $+ 77^\circ$ in *n*- HCl (amorphous *Ac*, $[\alpha]_D^{24} - 232.8^\circ$ in H_2O , and *Bz* derivative, $[\alpha]_D^{24} - 220.3^\circ$ in EtOH). Use of an excess of Na leads to much racemisation, which cannot in any case be entirely avoided. PhNCO and (III) in aq. NaOH give $\text{CO}(\text{NHPh})_2$ and dimethylcysteinephenylhydantoin, m.p. 219—220°, $[\alpha]_D^{23} - 131.3^\circ$ in CHCl_3 , reduced by Zn dust- AcOH to N-methylcysteinephenylhydantoin, m.p. 179—180°, $[\alpha]_D^{24} - 101.6^\circ$ in CHCl_3 . With CH_2O (III) gives N-methylthiazolidine-4-carboxylic acid [hydrochloride, m.p. 194° (decomp.), $[\alpha]_D^{24} - 119.2^\circ$ in H_2O], reaction being more facile than with cysteine (IV). The rate of decomp. of (II) and (III) by Na_2PbO_2 = that of (IV), but, as expected, there is no autocatalytic effect. R. S. C.

l-Amidocarbothionlactic acid and its anhydride. N. HELLSTRÖM (Arkiv Kemi, Min., Geol., 1938, 12, A, No. 20, 11 pp.).—l-(+)-Lactic acid gives l-amidocarbothionlactic acid (I), m.p. about 110—115° (sinters at about 100°), $[\alpha]_D^{20} + 16.6^\circ$ in EtOH , which consumes 2 I in acid solution with formation of $\text{NH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. (I) is stable in neutral, acid, or ammoniacal solution, but is racemised by alkali. Boiling in H_2O dehydrates (I) to l-4-keto-2-thio-5-methyltetrahydro-oxazole (II), m.p. 113.5—114.5°, $[\alpha]_D^{20} - 27.4^\circ$ in EtOH , which is indifferent to I. In H_2O or dil. acid (II) gives (I), reaction being unimol. in H_2O . Alkali successively racemises (II), converts it into dl-(I), and thence into $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ and HCNS . R. S. C.

Aliphatic carbodi-imides. I. E. SCHMIDT, F. HITZLER, and E. LAHDE [with R. HERBECK and M. PEZZATI] (Ber., 1938, 71, [B], 1933—1938).— $\text{CS}(\text{NHPr}^a)_2$ when shaken with yellow HgO in Et_2O at room temp. gives di-n-propylcarbodi-imide, b.p. 53—54°/10 mm. (yield 81%), which slowly decomposes at room temp. in diffused daylight. The following transitions are effected analogously: di-n-butylthiocarbamide, m.p. 64—65°, to di-n-butylcarbodi-imide, b.p. 84—85°/10 mm.; $\text{CS}(\text{NH}^i\text{Bu})_2$ to diisobutylcarbodi-imide, b.p. 71.5—72.5°/10 mm.; N-n-propyl-N'-allylthiocarbamide to n-propylallylcarbodi-imide, b.p. 54—55°/9 mm., which rapidly becomes yellow when preserved; diallylthiocarbamide to the unstable diallylcarbodi-imide, b.p. 58—59°/10 mm.; N-cyclohexyl-N'-allylthiocarbamide, m.p. 71—72°, to the unstable cyclohexylallylcarbodi-imide, b.p. 104—105°/10 mm.; N-cyclohexyl-N'-crotylthiocarbamide, m.p. 111—112.5° (in C_6H_6), to cyclohexylcrotylcarbodi-imide, b.p. 110.5—111.5°/10 mm.; N-β-hydroxyethyl-N-allylthiocarbamide, m.p. 77.5—78.5° (in C_6H_6), to β-hydroxyethylallylcarbodi-imide (2-allylimino-oxazolidine), b.p. 104—105°/10 mm.; dicyclohexylthiocarbamide to the cryst. dicyclohexylcarbodi-imide, b.p. 154—156°/11 mm. H. W.

Hydrogen cyanide; the tetrapolymer. E. GRYSKIEWICZ-TROCHIMOWSKI (J.C.S., 1938, 1466).—The arguments of Hinkel *et al.* (A., 1937, II, 433) are

criticised, and it is pointed out that in any case their proposed formula is tautomeric with that of the author (A., 1928, 745). F. J. G.

Bromo-derivatives of malononitrile. L. RAMBERG and S. WIDEQVIST (Arkiv Kemi, Min., Geol., 1938, 12, A, No. 22, 12 pp.).—Addition of $\text{CH}_2(\text{CN})_2$ to Br (2 mols.) and a metallic bromide in H_2O gives complex salts, $\text{XBr}_2\cdot 4\text{CBr}_2(\text{CN})_2$ [$\text{X} = \text{K}, \text{Na}, \text{Li}$ (impure), and NH_4], whence $\text{CBr}_2(\text{CN})_2$ (I) is obtained by sublimation in vac. CuBr_2 leads, however, to a complex salt, yielding $\text{NH}_2\cdot\text{CO}\cdot\text{CBr}_2\cdot\text{CN}$, m.p. 126–127°. The K salt is used to separate (I) from reaction mixtures. With 1 mol. of Br $\text{CH}_2(\text{CN})_2$ always gives some (I). However, (I) and $\text{CH}_2(\text{CN})_2$ give $\text{CHBr}(\text{CN})_2$ (II), m.p. 64.5–65.1°, which is obtained in 82% yield by brominating to (I) and then adding an extra mol. of $\text{CH}_2(\text{CN})_2$. The reaction, $(\text{II}) + 2\text{HI} \rightarrow \text{CH}_2(\text{CN})_2 + \text{HBr} + 2\text{I}$, is used to determine (II). Addition of I to (II) in COMe_2 gives 68% of $\alpha\gamma\gamma$ -tetracyano- $\beta\beta$ -dimethylpropane, m.p. 208–209°. (I) and NPhMe_2 give $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NMe}_2$. R. S. C.

Decomposition of diazo-ketones. C. GRUNDMANN [with H. TRISCHMANN] (Annalen, 1938, 536, 29–36; cf. A., 1936, 1233).—Dry decomp. of diazo-ketones in presence of CaO , Cu , Ag , or SnO_2 gives N_2 and ill-defined resins. Better results are obtained with CuO in inert media whereby diacylethylenes are obtained. The yield depends greatly on the nature of the solvent. Thus CHBzN_2 gives *trans*- $\alpha\beta$ -dibenzoyl-ethylene, m.p. 110°, in 0%, 0%, 0%, 45%, 51%, 39%, and 65% in Et_2O , CHCl_3 , EtOAc , C_6H_6 , PhMe , xylene, and light petroleum, b.p. 70–80°, respectively. Similarly the diazo-ketone of $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ affords $\alpha\beta$ -diphenylacetylene, m.p. 105–106°, the yellow colour of which indicates the partial existence in the dienolic form which is not confirmed by the Zerevitinov–Roth method. CHAcN_2 yields $\alpha\beta$ -diacetyl-ethylene, m.p. 77°, which readily volatilises in air. α -Diazononadecan- β -one yields $\alpha\beta$ -distearoyl-ethylene, m.p. 104°. CPhBzN_2 does not give the expected *s*-dibenzoylstilbene but resins and a small amount of benzoylphenylketazine, m.p. 205°. The thermal, non-catalysed decomp. of CHBzN_2 yields *cis*-1 : 2 : 3-tribenzoylcyclopropane, m.p. 217°. H. W.

Direct alcoholysis of adrenal phosphatides. G. Y. SHINOWARA and J. B. BROWN (Oil and Soap, 1938, 15, 151–152; cf. A., 1931, 249).—Adrenal phosphatides (ox) are converted directly into esters with *n*-alcohols (C_{1-5}) and 5% HCl or 7.5–12% H_2SO_4 . Pr^a , m.p. 223–224°, Bu^a , m.p. 222–223°, and *n*-amyl, m.p. 221.5–222.5°, octabromoarachidones are prepared. A. T. P.

Action of Grignard's reagents on heptachloropropane. M. REBEK and G. MANDRINO (Österr. Chem.-Ztg., 1938, 41, 363–364).—The reaction between heptachloropropane and MgMeI proceeds $\text{C}_3\text{HCl}_7 + \text{MgMeI} = \text{C}_3\text{Cl}_6 + \text{MgICl} + \text{CH}_4$ and (?) $\text{C}_3\text{HCl}_7 + 2\text{MgMeI} = \text{C}_3\text{HCl}_5 + 2\text{MgICl} + \text{C}_2\text{H}_6$. The gaseous product from C_3HCl_7 and MgEtI is mainly butane, whilst under similar conditions C_2H_6 is derived from C_2HCl_5 and MgMeI . H. W.

Reducing action of the *tert*-butyl Grignard reagent on acyl chlorides. F. L. GREENWOOD,

F. C. WHITMORE, and H. M. CROOKS (J. Amer. Chem. Soc., 1938, 60, 2028–2030).—Adding MgBu^tCl (prep. described) (1 mol.) to Bu^tCOCl (5 mols.) in Et_2O at -10° gives 32.4% of addition and 8% of reduction products, COBu^t_2 , *neopentyl pivalate*, b.p. 164–165°/740 mm., and pivalic anhydride being isolated. However, adding Bu^tCOCl (1 mol.) to MgBu^tCl (4 mols.) at 40° gives 1.5% of addition and 94% of reduction products, Bu^tOH , $\text{CHBu}^t_2\cdot\text{OH}$ (1.5%), and C_2Me_6 . Adding Pr^iCOCl (1 mol.) to MgBu^tCl (5 mols.) gives 63% of addition ($\text{CHPr}^i\text{Bu}^t\cdot\text{OH}$) and 20% of reduction product (Bu^tOH). Adding Pr^iCOCl (1 mol.) to MgBu^tCl (4 mols.) gives 71% of addition [$\beta\beta$ -dimethylhexan- γ -ol (α -naphthylurethane, m.p. 113–114°)] and 9% of reduction product (Bu^tOH). In all cases 2 equivs. of $\text{CMe}_2\cdot\text{CH}_2$ are formed for each equiv. of ketone reduced. R. S. C.

Action of magnesium *tert*-butyl chloride on *tert*-butylacetyl [β -methylvaleryl] chloride. F. C. WHITMORE and J. W. HEYD (J. Amer. Chem. Soc., 1938, 60, 2030–2031).— $\text{CH}_2\text{Bu}^t\cdot\text{COCl}$ (1 mol.) with MgBu^tCl (>2 mols.) in Et_2O gives 71% of $\text{CH}_2\text{Bu}^t\cdot\text{CHBu}^t\cdot\text{OH}$, 1% of $\text{CH}(\text{CH}_2\text{Bu}^t)_2\cdot\text{OH}$, and, in some cases, 5% of *tert*-butylneopentylcarbonyl β -methylisovalerate (I), b.p. 90°/5 mm. MgBu^tCl (1 mol.) with $\text{CH}_2\text{Bu}^t\cdot\text{COCl}$ (1 mol.) gives 17% of (I) and 51% of *Bu*^{*neopentyl ketone*}, b.p. 161°/728 mm. [2 : 4-dinitrophenylhydrazones, m.p. 123.5–124.5°, formed with difficulty; resists $\text{Al}(\text{OPr}^i)_3$; no oxime or semicarbazone]. (I) is also obtained by esterification, but resists KOH – EtOH at 90–100°. R. S. C.

Preparation of aluminium methyl chlorides. V. F. HNZIDA and C. A. KRAUS (J. Amer. Chem. Soc., 1938, 60, 2276).—Prep. in excellent yield of a 1 : 1 mixture of AlMeCl_2 and AlMe_2Cl from MeCl and Al and a trace of AlCl_3 or I as catalyst is detailed. The halides are separated by distillation or by heating with an excess of NaCl , from which AlMe_2Cl distils, the compound, $\text{AlMeCl}_2\cdot\text{NaCl}$, being non-volatile. AlEtCl_2 and AlEt_2Cl are similarly prepared. R. S. C.

Organic derivatives of scandium and of yttrium. V. M. PLETZ (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 27–28; cf. Dennis *et al.*, A., 1934, 761).—*ScEt}_3* etherate, prepared (70% yield) in N_2 by the addition of ScCl_3 to MgEtBr in ice-cold Et_2O , is a yellow liquid, b.p. 170–172°. With H_2O or EtOH it yields probably *ScEt}_2\cdot\text{OH}, with $\text{Br}\cdot\text{H}_2\text{O}$, *ScEt}_2\text{Br}. Prep. and properties of *YEt}_3* etherate, b.p. 222–225°, are similar. Grosse's theory of alkyl compounds requires revision. I. MoA.**

Complex compounds of diguanide with trivalent metals. II. Chromium diguanides. III. Chromium phenyldiguanides. P. RAY and N. N. GHOSH. IV. Chromium bisdiguanides. P. RAY and H. SAHA (J. Indian Chem. Soc., 1938, 15, 347–349, 350–352, 353–358; cf. A., 1938, II, 176).—II. Cr trisdiguanide hydrochloride and an appropriate inorg. salt give by double decomp. the ferricyanide, cobalticyanide, chromithiocyanate, and cobaltinitrite of type, $[\text{CrR}_3]\text{X}$, in which $\text{R} = \text{NH}[\text{C}(\text{NH})\cdot\text{NH}_2]_2$, the chloronitroprusside, $[\text{CrR}_3]\text{Cl}[\text{Fe}(\text{NO})(\text{CN})_5]$, hydrozomercuri-iodide, $\text{OH}[\text{CrR}_3](\text{HgI}_3)_2$, and chlorobismuthi-

iodide, $\text{Cl}[\text{CrR}_3](\text{BiI}_4)_2$. Tetrabasic complex acids gave indefinite material.

III. Existence of the complex ion,

$\text{Cr} \left[\begin{array}{c} \text{N}:\text{C}(\text{NH}_2) \\ \text{NHP} \cdot \text{C}(\text{NH}) \end{array} \right]_3 \text{NH}$, is proved by formation of salts with 3 equivs. of acid, the tribasicity being proved by the Λ and the mol. wt. by cryoscopy in H_2O . $\text{NH}:\text{C}(\text{NH}_2) \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{NHP}$, CrCl_3 , and aq. NaOH give *Cr trisphenyldiguanide trihydroxide*, $[\text{CrR}'_3](\text{OH})_3$, [in which $\text{R}' = \text{NHP} \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot \text{C}(\text{N}) \cdot \text{NH}_3^+$], which loses $2\text{H}_2\text{O}$ at 110° , becomes anhyd. at 135° , and slowly polymerises in EtOH . The base yields the *chloride, bromide, iodide, nitrate, chromate, and sulphate* of type, $[\text{CrR}'_3]\text{X}_3$.

IV. With aq. $(\text{NH}_4)_2\text{SO}_4$ $[\text{CrR}_3](\text{OH})_3$ (I) yields *Cr hydroxoquobisdiguanide sulphate*, $[\text{CrR}_2\text{OH}, \text{H}_2\text{O}]\text{SO}_4$ [stable at 120° ; with warm NaOH regenerates (I)]. $\text{BaCl}_2 \cdot \text{NH}_4\text{Cl}$ converts this into the corresponding *chloride*, $+\text{H}_2\text{O}$ and anhyd., which over H_2SO_4 loses H_2O to give the *salt*, $[\text{CrR}_2, \text{OH}, \text{Cl}]\text{Cl}$, which in air regenerates the hydrate. The *bromide, iodide, nitrate, thiosulphate, chromate, camphorsulphonate*, and *dihydroxide* (loses $3\text{H}_2\text{O}$ at 105 – 110° with partial decomp.) are prepared. Further hydrolysis also occurs, but no definite products, except finally $\text{Cr}(\text{OH})_3$, are isolated. R. S. C.

Thermal decomposition of lead di-*n*-butyl dichloride. D. P. EVANS (J.C.S., 1938, 1466).—At 130° , PbBu_2Cl_2 decomposes to $\text{PbCl}_2 + \text{BuCl} + \text{PbBu}_3\text{Cl}$. F. J. G.

Physical properties and chemical constitution. III. *cyclo*-Pentane, -hexane, and -heptane, and derivatives. Multiplanar structure of the methylcyclohexane ring. A. I. VOGEL (J.C.S., 1938, 1323—1338; cf. A., 1935, 65).—Surface tensions and densities over a range of temp., and vals. of η for the *C*, *D*, *F*, and *G* lines at 20° are measured for pure *cyclo*- and methylcyclo-pentane and -hexane, cycloheptane, and their related ketones, alcohols, and unsaturated hydrocarbons, and also for a no. of CH_2 compounds. Parachors, mol. refractivities, dispersions, and mol. refraction coeffs. are evaluated. In general, the CO-derivative is converted by $\text{Na-Et}_2\text{O-H}_2\text{O}$ into the $\cdot\text{CH}(\text{OH})\cdot$, dehydrated by P_2O_5 to the unsaturated hydrocarbon, which is then reduced with H_2 -Pt (Adams). *cyclo*Heptanol (I), b.p. $185^\circ/761$ mm., however, affords *cyclo*heptene (II), b.p. 114 – $115^\circ/774$ mm., and a methylcyclohexene, proved by reduction in EtOH (cf. Harries and Tank, A., 1908, i, 517). (I) and PBr_3 give *cyclo*heptyl bromide, b.p. $62.5^\circ/6$ mm., which with KOH-EtOH for 5 hr. yields (II) and (?) *cyclo*heptyl Et ether. 1-Methyl- and 2-methyl-, b.p. $165^\circ/762$ mm., -*cyclo*hexanols afford mainly 1-methyl- Δ^1 - (III), b.p. $110^\circ/769$ mm. and Δ^2 -, b.p. $106^\circ/758$ mm., -*cyclo*hexenes (cf. Wallach, A., 1908, i, 425) respectively, whilst 3-methyl-, b.p. $172^\circ/763$ mm., and 4-methyl-, b.p. $172^\circ/763$ mm., -*cyclo*hexanols yield mainly 1-methyl- Δ^3 -*cyclo*hexene (IV), b.p. $105^\circ/761$ mm., $105.5^\circ/765$ mm. (III) is reduced satisfactorily only in absence of solvent and after 84 hr.

Reduction of (III) or (IV) affords the same stable methylcyclohexane (A), b.p. 100.4 – $100.7^\circ/773$ mm.

An unstable methylcyclohexane (B), b.p. 100.2 – $100.4^\circ/768$ mm., is obtained from methyl- Δ^2 -cyclohexene, converted at room temp. in 7 days or at 40 – 50° in 2–3 hr., into a stable form (C) (cf. Smittenberg and Hoog, Chem. & Ind., 1938, 753). These three forms of methylcyclohexane (V) provide the first experimental evidence for the multiplanar structure of the cyclohexane ring; preponderance of one or other of the multiplanar forms may be a partial explanation of the recorded differences in physical properties of (V) when prepared in varying manner. One of the acetylcyclohexanes described by Zelinski and Turova-Pollak (Annalen, 1934, 508, 115) contains, or is, probably a methylacetylcyclopentane. The following data are new or have been disputed. Many other physical consts. are recorded: *cyclopentanone*, b.p. $129^\circ/756$ mm. (3-methyl-, b.p. $144^\circ/770$ mm.); *cyclohexanone*, b.p. $155^\circ/763.5$ mm.; 2-methyl-, b.p. $165^\circ/764$ mm., 3-methyl-, b.p. $169^\circ/762$ mm., and 4-methyl-, b.p. $170^\circ/761$ mm., -*cyclo*hexanone; *cycloheptanone*, b.p. $180^\circ/760$ mm.; *trans*- β -ketodecahydronaphthalene, b.p. $117^\circ/16$ mm.; *trans*-hexahydro- β -hydrindene, b.p. $92^\circ/13$ mm.; methylenecyclopentane, b.p. 75 – $76^\circ/760$ mm., and -hexane, b.p. 102 – $103^\circ/764$ mm.; 1-methyl-3-, b.p. 123 – $124^\circ/762$ mm., and 1-methyl-4-, b.p. 124 – $125^\circ/772$ mm., -methylenecyclohexane; 2-methylene-*trans*-decahydronaphthalene, b.p. 82 – $82.5^\circ/10$ mm., and -hexahydrohydrindene, b.p. 59 – $60^\circ/9.5$ mm.; *cyclo*-, b.p. $139^\circ/760$ mm., -*cyclopentylcyclo*-, b.p. $100^\circ/3$ mm., and 3-methylcyclo-, b.p. $152^\circ/766$ mm., -pentanols; *cyclo*hexanol, b.p. $159^\circ/755$ mm. *cyclo*pentene, b.p. $44.3^\circ/761$ mm.; 1-methyl- Δ^2 -*cyclo*pentene, b.p. $72^\circ/770$ mm.; *cyclo*hexene, b.p. $83^\circ/777$ mm.; *cyclo*-, b.p. 48.4 – $48.6^\circ/763$ mm., and methylcyclo-, b.p. 70.9 – $71.0^\circ/751$ mm., -pentanes; *cyclo*-hexane, b.p. $80.2^\circ/763$ mm., and -heptane, b.p. 117.5 – $118^\circ/758$ mm. Me_2 , b.p. $139^\circ/4$ mm., and Et_2 , b.p. $145^\circ/4$ mm., 2-methylcyclohexane-1:1-diacetate. A. T. P.

Carotenoids. V. Gazanixanthin. K. SCHÖN (Biochem. J., 1938, 32, 1566—1570).—Chromatographic adsorption of the saponified lipid extracts of *Gazania rigens* on Al_2O_3 yielded a xanthophyll, *gazanixanthin*, $\text{C}_{40}\text{H}_{54}\text{O}$ or $\text{C}_{40}\text{H}_{56}\text{O}$, m.p. 136 – 137° (acetate, m.p. 83 – 85°), similar in physical and chemical properties to rubixanthin; it is hence probably related to γ -carotene (I). Rubixanthin, lutein, and "leaf xanthophyll" were isolated in the cryst. state from *Gazania* extracts, with another unknown carotenoid with the same absorption spectrum as (I). T. F. D.

Cryptodienes and pseudodienes. E. MAMELI (Gazzetta, 1938, 68, 428—443).—Theoretical. Cryptodienes are aromatic compounds in which *p*-substituents have induced capacity for 1:4- or $\alpha\delta$ -addition (e.g., quinones; $\text{CHPh}:\text{CH}_2$ with azoesters; Ph_2 with Li; *p*- $\text{C}_6\text{H}_4\text{Ph}_2$ with Na; and various condensed systems). Pseudodienes are C_3 or C_4 ring systems with $\text{CH}:\text{CHR}$ as substituent, which cannot give rise to a diene, but yet react as if containing a conjugated system (e.g., α -pinene and other terpenes). E. W. W.

Substitution in the benzene nucleus. J. C. MCGOWAN (Chem. and Ind., 1938, 933—934).—If it is assumed that the resonance forms of C_6H_6 include some, possibly very little, of those in which 2 or 3 H are shared between neighbouring C, then the anticipated effect of substituents explains the rules previously formulated (A., 1936, 1238). R. S. C.

Mixed laterally-halogenated toluenes. L. S. HEBLE, D. R. NADKARNI, and T. S. WHEELER (J.C.S., 1938, 1322—1323).— CH_2PhCl and Br at 100° afford CH_2PhBr , $CHPhBr_2$, and ω -chloro- ω -bromotoluene (I) b.p. $92-95^\circ/2-3$ mm. $CHPhCl_2$ and Br at $120-140^\circ$ yield $\omega\omega$ -dichloro- ω -bromotoluene, b.p. $88-94^\circ/1$ mm., and ω -chloro- $\omega\omega$ -dibromotoluene, b.p. $98-103^\circ/1$ mm. (I) and Br at 135° for 6 hr. give $CHPhBr_2$ and more Br at 160° for a further 6 hr. gives $CPhBr_3$, new m.p. 60° (cf. Hunter and Edgar, A., 1932, 717). CH_2PhBr and Cl_2 at 110° for 4 hr. afford (I) and at 150° for 7 hr., then 160° for 4 hr., give $CPhCl_2Br$ and $CPhCl_3$. Thus under certain conditions, Cl and Br displace each other from the toluene side-chain. Determination of side-chain halogen (cf. A., 1938, II, 211) is based on the observation that anhyd. HCO_2H and di- and tri- ω -halogenated toluenes give $PhCHO$ and $BzOH$ respectively, HX and CO being evolved. A. T. P.

Acetylene derivatives. X. Transformation of 2:2'-dinitrotolan into a nitroso-compound by unsymmetrical halogen addition. P. RUGGLI, H. ZAESLIN, and F. LANG (Helv. Chim. Acta, 1938, 21, 1240—1249).—2:2'-Dinitrotolan (I) (1 mol.) and Cl_2 (1 mol.) in CCl_4 do not react during 40 hr. at room temp. or 3 hr. at 100° . By excess of Cl_2 in $CHCl_3$ (I) is transformed at room temp. into $\beta\beta$ -dichloro- α -keto- α -2-nitrosophenyl- β -3': 5'-dichloro-6'-nitrophenylethane (II) (also $+1C_6H_6$), m.p. 138° when heated rapidly. The change is probably (I) \rightarrow

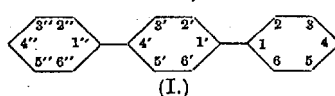
$NO_2 \cdot C_6H_4 \cdot \dot{C} \cdot CCl_2 \cdot C_6H_4 \cdot NO_2 \rightarrow$
 $NO \cdot C_6H_4 \cdot CO \cdot CCl_2 \cdot C_6H_4 \cdot NO_2 \rightarrow$
 $NO \cdot C_6H_4 \cdot CO \cdot CCl_2 \cdot C_6H_4 \cdot Cl_2 \cdot NO_2$ (II) is oxidised by CrO_3 in $AcOH$ to $\beta\beta$ -dichloro- α -keto- α -2-nitrophenyl- β -3': 5'-dichloro-6'-nitrophenylethane, m.p. 142° , and thence by conc. HNO_3 to o - $NO_2 \cdot C_6H_4 \cdot CO_2H$. Boiling C_5H_5N containing 10% of H_2O transforms (II) into o - $NO_2 \cdot C_6H_4 \cdot CO_2H$ and 3:5-dichloro-2-nitrobenzylidene chloride, m.p. 45° , identical with the product obtained from 2:3:5- $NO_2 \cdot C_6H_3Cl_2 \cdot CHO$. Warm $EtOH$ - $AgNO_3$ and (II) give $AgCl$, much resin, and a little dichloronitronitrosobenzil, m.p. 179° , and a compound, $C_{14}H_6O_4N_2Cl_2$ or $C_{14}H_8O_4N_2Cl_2$, m.p. 159° . With NaI in $COMe_2$ (II) gives a yellow substance, m.p. 177° . H. W.

Syntheses of polyenes with the help of acetylene and diacetylene. R. KUHN and K. WALLENFELS (Ber., 1938, 71, [B], 1889—1899).— C_2H_2 is slowly passed into $MgEtBr$ and $CHPh:CH:CHO$ is added to the product, giving $\alpha\theta$ -diphenyl- Δ^{an} -dien- Δ^8 -ine- γ -diol, two forms, m.p. 162° and 119° respectively, the latter of which is hydrogenated ($Pd-BaSO_4$ in abs. $EtOH$) to $\alpha\theta$ -diphenyl- Δ^{an} -octatriene- γ -diol, m.p. $107-110^\circ$; this is transformed by P_2I_4 in Et_2O followed by $2N-NaOH$ or by VCl_2 and conc. HCl into $\alpha\theta$ -diphenyl- Δ^{an} -octatetraene, m.p. 233° . $CH_2Ph:CHO$ similarly gives α - ζ -diphenyl-

Δ^7 -hexinene- $\beta\epsilon$ -diol, m.p. $92-93^\circ$, hydrogenated to a non-cryst. material transformed by Ac_2O and $KHSO_4$ into α - ζ -diphenyl- Δ^{an} -hexatriene (I), m.p. 201° . Diacetylene and $PhCHO$ give α - ζ -diphenyl- $\Delta^{8\beta}$ -hexatriene- α -diol, m.p. crude $81-85^\circ$, from which a fraction, m.p. $131-132.5^\circ$, was separated but with which the complete separation of the *r*- and *meso*-forms does not appear to have been effected; it is hydrogenated ($Pd-BaSO_4$ in $EtOH$) to (I) or, under other conditions, to isohydrocinnamoin, m.p. 149° . $\alpha\alpha\delta\delta$ -Tetraphenyl- Δ^8 -butinene- $\alpha\delta$ -diol is partly hydrogenated and then transformed by boiling $AcOH$ into tetraphenylbutatriene, m.p. 237° , whereas partial hydrogenation followed by treatment with P_2I_4 in Et_2O gives $\alpha\alpha\delta\delta$ -tetraphenylbutadiene, m.p. $201-202^\circ$. $\alpha\alpha\zeta\zeta$ -Tetraphenyl- $\Delta^{8\beta}$ -hexadiene- α -diol is completely hydrogenated to $\alpha\alpha\zeta\zeta$ -tetraphenylhexane- α -diol, m.p. 211° , and partly hydrogenated to $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{8\beta}$ -hexadiene- α -diol, m.p. 147° , whence $\alpha\alpha\zeta\zeta$ -tetraphenyl- Δ^{an} -hexatriene, m.p. $206-207^\circ$. Partial hydrogenation and subsequent treatment with P_2I_4 transforms didiphenylenehexadiene-diols into α - ζ -didiphenylene- Δ^{an} -hexatriene, m.p. $331-332^\circ$. Successive treatments of $MgEtBr$ with C_2H_2 and $CHPh:CMc:CHO$ lead to $\alpha\theta$ -diphenyl- $\beta\eta$ -dimethyl-octa- Δ^{ac} -diene- Δ^8 -ine- γ -diol, m.p. $86-89^\circ$, semi-hydrogenated ($Pd-BaSO_4$ in $EtOH$) to $\alpha\theta$ -diphenyl- $\beta\eta$ -dimethyl- Δ^{an} -octatriene- γ -diol, m.p. $94-95^\circ$; semi-hydrogenation followed by treatment with $CrCl_2$ in Et_2O leads to $\alpha\theta$ -diphenyl- $\beta\eta$ -dimethyl- Δ^{an} -octatetraene, m.p. 176.5° , which gives a blood-red colour with conc. H_2SO_4 and a red-violet solution with $SbCl_3$ in $CHCl_3$. $CHPh:CH:COMe$ and Mg_2 diacetylenyl bromide afford $\alpha\kappa$ -diphenyl- $\gamma\theta$ -dimethyldeca- Δ^{ac} -diene- Δ^8 -di-ine- $\gamma\theta$ -diol, m.p. (indef.), 122° , which gives a violet solution in conc. H_2SO_4 and an indigo-blue colour with $SbCl_3$ in $CHCl_3$. Partial hydrogenation and treatment with $CrCl_2$ converts it into $\alpha\kappa$ -diphenyl- $\gamma\theta$ -dimethyl- Δ^{an} -decapentaene, m.p. $196-197^\circ$. cycloHexanone and the Mg compound from diacetylene yield $\alpha\delta$ -dicyclohexan-1-olyl- Δ^8 -butadiene, m.p. 170° , converted by $KHSO_4$ at 150° into $\alpha\delta$ -di- Δ -cyclohexenyl- Δ^8 -butadiene, m.p. $62.5-63^\circ$, which absorbs 6 H_2 (PtO_2 in $AcOH$).

H. W.

Terphenyl series. I. *p*-Terphenyl, nitro-, amino-, and halogeno-*p*-terphenyls. H. FRANCE, I. M. HEILBRON, and D. H. HEY (J.C.S., 1938, 1364—1375).—The literature of



p-terphenyl (I) is reviewed. $C_6H_4Ph \cdot NHAc$, and diacetyl-, diformyl- ($+P_2O_5$), and di-*n*-propionyl-, m.p. $289-291^\circ$, *p*-phenylenediamine and nitrous fumes in $AcOH$ - Ac_2O at 8° afford respectively 4-nitrosoacetamidodiphenyl (II), m.p. 98° (explosive decomp.), dinitroso-diacetyl- (III), m.p. $124-125^\circ$ (explosive decomp.) [best for prep. of (I), 55—60% yield], diformyl-, violent decomp. at 132° , and di-*n*-propionyl-, explodes at 110° , *p*-phenylenediamines, which with C_6H_6 at 20° (35° ; $50-55^\circ$, then reflux; 45°) for 12 hr. ($2:2:2$) all yield (I). This and HNO_3 (d 1.5) in Ac_2O at 0° , then at $45-50^\circ$ for 1 hr., afford 4:4'-dinitro-*p*-terphenyl (IV), m.p. $272-273^\circ$, obtained also from (III) and $PhNO_2$ at 25° or from (V) and HNO_3 - $AcOH$ at

100° for 1 hr. (IV) and $\text{CrO}_3\text{-AcOH}$ afford $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. Nitration of (I) in AcOH at 100° affords (IV) and 4:2':4''-trinitro- p -terphenyl, m.p. 193—194°, also obtained from (I) and HNO_3 (d 1.5) or $\text{H}_2\text{SO}_4\text{-HNO}_3$ at 45—50° for 5 hr., or from (IV) and $\text{HNO}_3\text{-AcOH}$ at 100° for $\frac{1}{4}$ hr. (II) and PhNO_2 at 20° for 48 hr. give 4-nitro- (V), m.p. 211—212°, and 2-nitro- (VI), m.p. 127—128°, - p -terphenyl. 4-Nitro- and 2-nitro-, m.p. 152—153°, -4'-acetamidodiphenyl yield 4-nitro-4'-nitroso-, m.p. 106° (decomp. explosively), and 2-nitro-4'-nitroso-, m.p. 85—87° (decomp.), -acetamidodiphenyl, converted by C_6H_6 at 20° for 24 hr. into (V) and (VI), respectively. (VI) and $\text{CrO}_3\text{-AcOH}$ for 4 hr. give 2-nitrodiphenyl-4'-carboxylic acid. (V) and (VI) and $\text{SnCl}_2\text{-HCl-EtOH}$ for 6 hr. afford 2-amino- (VII), m.p. 159—160° (Ac derivative, m.p. 125—126°), and 4-amino- p -terphenyl, respectively. The NO -derivative of 3:4'-dinitro-4'-acetamidodiphenyl and C_6H_6 at 20° give 4:3'-dinitro- p -terphenyl, m.p. 174—175°, which with $\text{HNO}_3\text{-AcOH}$ at 100° affords the above $(\text{NO}_2)_3$ -derivative. 2-Nitrodinitrosodiacyetyl-1:4-phenylenediamine and C_6H_6 afford 3-nitro-4'-acetamidodiphenyl; 2:3-dinitrodiaacyetyl-1:4-phenylenediamine does not form a NO -derivative. (II) and PhCl at 20° give 2-chloro-, m.p. 110—111° [also from (VII) by diazo-reaction], 3-chloro-, m.p. 136—137°, and 4-chloro-, m.p. 220—221°, - p -terphenyl, whilst PhBr similarly affords 2-bromo- (VIII), m.p. 86—88°, 3-bromo-, m.p. 147—148°, and 4-bromo- (IX), m.p. 231—232°, - p -terphenyl, the 3-derivatives being in smallest amount. The reactions may involve free radicals. (VIII) and $\text{CrO}_3\text{-AcOH}$ give 2-bromodiphenyl-4'-carboxylic acid. (I) and Br in AcOH (trace of I) at 100° for 1 hr. yield (IX) and 4:4'-dibromo- p -terphenyl. 4-Bromo-, m.p. 91—92° (decomp.), and 4-iodo-, m.p. 90—91° (decomp.), -4'-nitrosoacetamidodiphenyl and C_6H_6 at 30° (40°) give (IX) and 4-iodo- p -terphenyl, m.p. 246—247°, respectively. 4-Iodo-4'-acetamidodiphenyl melts at 246—247°. (III) and molten $p\text{-C}_6\text{H}_4\text{Cl}_2$ at 50—55°, then at 90° for 2 hr., yield 2:5:2'':5''-tetrachloro- p -terphenyl, m.p. 203—204°. $o\text{-C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{Cl}$ and PhMe in 40% aq. NaOH afford bromomethyldiphenyls, oxidised by $\text{CrO}_3\text{-AcOH}$ for 12 hr. to 2-bromodiphenyl-2'-carboxylic acid and an isomeride (X); the former and conc. H_2SO_4 at 45—50° for $\frac{1}{4}$ hr. yield 4-bromofluorenone, m.p. 127—128°. Similarly $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{N}_2\text{Cl}$ and PhBr give 2- and 4-bromo-4'-methyldiphenyl, the former being oxidised to (X), i.e., 2-bromodiphenyl-4'-carboxylic acid. A. T. P.

Tar hydrocarbons. II. Derivatives of 2:3-dimethylnaphthalene. E. A. COULSON (J.C.S., 1938, 1305—1310; cf. A., 1935, 334).—2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$ (I) and conc. H_2SO_4 at 40—50° or ClSO_3H at 0—10°, in CCl_4 or decahydronaphthalene, afford the 5-sulphonic acid (Ba salt; *sulphonamide*, m.p. 208°) (ClSO_3H gives also some 6-isomeride), converted through the Na salt (+2 H_2O) and KOH at 290—310° into 6:7:1- $\text{C}_{10}\text{H}_5\text{Me}_2\cdot\text{OH}$ (II), m.p. 140°, b.p. 240—244°/2 mm. Hydrogenation ($\text{C-MoO}_3\text{-S}$, 350—360°/100 atm.) of (I) gives 1:2:3:4-tetrahydro-6:7-dimethylnaphthalene (III), m.p. 10°, b.p. 244—246°; cis- and trans-1:2:3:4-tetrahydro-2:3-dimethylnaphthalene, A form, has m.p. -8° to -5°, b.p. 222—

224°, and B form, m.p. 4—8°, b.p. 229—231°, purified through their sulphonic acids and H_{10} -derivatives of (I). (III) and conc. H_2SO_4 at <60° for $\frac{1}{2}$ hr. give the 5-sulphonic acid [Na (+7 H_2O) and Ba (+6 H_2O) salts; *sulphonamide*, m.p. 135°], which with KOH and a little H_2O at 300—330° for 10 min. affords some (II) and 6:7:2- $\text{C}_{10}\text{H}_5\text{Me}_2\cdot\text{OH}$ (IV), m.p. 160°; the action of aq. KOH in H_2 at 350°/20 atm. for 3 hr. gives a neutral oil and S , and in N_2 at 320—350° for $\frac{1}{2}$ to 1 hr. affords (I) and (IV) only. (III) and HNO_3 (d 1.52) in Ac_2O at <5° give the 5- NO_2 -compound, reduced (Zn-HCl) to the 5- NH_2 -derivative, b.p. 126—128°/2 mm., 154—156°/15 mm. (Ac derivative, m.p. 125°). (III) and KMnO_4 yield pyromellitic acid, m.p. 264° (decomp.). The A and B forms above and conc. H_2SO_4 yield the respective 6-sulphonic acids, A [Ba salt (+6 H_2O); *sulphonamide*, m.p. 210—211°] and B [Na (+2 H_2O), Ba salts; *sulphonamide*, m.p. 143°], converted by KOH at 325—330° for 10 min. into the 1:2:3:4-tetrahydro-2:3-dimethyl-6-naphthols, form A , b.p. 122—124°/2 mm., form B , b.p. 130—132°/2 mm., respectively. In the latter case some (IV) is formed, obtained also from either form of naphthol and Se at 310°. The formation of both *sulphonamides*, m.p. 210—211° and 143°, from either Na *sulphonate* A or B is explained by possible interconversion during prep. The unstable *phenylhydrazone*, m.p. 120° (decomp.), of 1-keto-1:2:3:4-tetrahydro-6:7-dimethylnaphthalene (V) (A., 1933, 601) [2:4-dinitrophenylhydrazone, m.p. 286° (decomp.)] loses NH_3 in boiling AcOH to give 1:2-(4':5'-dimethylbenz)-3:4-dihydrocarbazole, m.p. 208°. (V) and Br-CS_2 at room temp. afford the 2- Br -derivative, m.p. 102.5° (more Br gives the 2:2- Br_2 -derivative, m.p. 135°), which loses HBr in boiling anhyd. NEt_2Ph for 1 hr. to yield (II). A. T. P.

Polycyclic aromatic hydrocarbons. XVIII. General method for synthesis of 3:4-benzphenanthrene derivatives. C. L. HEWETT (J.C.S., 1938, 1286—1291; cf. A., 1936, 835; B., 1937, 215, and following abstract).—1:2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{CH}_2\cdot\text{CN}$ and Na-EtOH-PhCHO afford α -2'-(1'-bromonaphthyl)-cinnamionitrile, m.p. 105—105.5°, hydrolysed by 50% H_2SO_4 or KOH-EtOH to the *cinnamic acid*, m.p. 206—207° (poor yield), obtained more readily from 1:2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{CH}_2\cdot\text{CONa}$ (I) and PhCHO in Ac_2O at 130—140° for 7 hr., and cyclised by fusion with KOH at 230—240° for 5 min. to 3:4-benz-10-phenanthroic acid, m.p. 244—245°. o -, m -, and p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$, in place of PhCHO as above, yield α -2'-(1'-bromonaphthyl)- β - o -, m.p. 233—235°, - m -, m.p. 204—205°, and - p -, m.p. 234—235°, *tolylacrylic acids*, respectively, cyclised to 8-, m.p. 269—270°, 7- (5-?), m.p. 243—244°, and 6-methyl-, m.p. 274—275°, -3:4-benz-10-phenanthroic acids, which are decarboxylated by $\text{C}_9\text{H}_7\text{N-Cu-bronze}$ at 250—260° for 1 hr. to the corresponding 8-, m.p. 65—66° (*picrate*, m.p. 107—108°), 7-, m.p. 54—54.5° (*picrate*, m.p. 134—134.5°), and 6-methyl-, m.p. 80—81° (*picrate*, m.p. 118—118.5°) -3:4-benzphenanthrenes. α - $\text{C}_{10}\text{H}_7\cdot\text{CHO}$ similarly yields α -2-(1-bromonaphthyl)- β -1'-naphthylacrylic acid (II), m.p. 267—268°, and a substance, m.p. 187—188°, stable to KOH at 230—240°. (II) is cyclised (KOH) to 1:2:5:6-dibenz-9-phenanthroic

acid, m.p. 309—310°, decarboxylated to 1:2:5:6-dibenzphenanthrene, m.p. 126—127° (picrate, m.p. 126.5—127°). 6-Acetyltetrahydronaphthalene and NaOCl afford 1:2:3:4-tetrahydro-6-naphthoic acid; the corresponding anilide, new m.p. 146—147°, and PCl_5 in $\text{C}_2\text{H}_5\text{Cl}_4$ at 150° for $\frac{1}{2}$ hr. give the iminochloride, converted by $\text{SnCl}_2\text{--HCl--Et}_2\text{O}$ at 0° for 4 hr., then at room temp. for 12 hr., into a stannichloride complex, hydrolysed by dil. HCl to 1:2:3:4-tetrahydro-6-naphthaldehyde (semicarbazone, new m.p. 228°). The latter and (I) (Perkin condensation) yield α -2-(1-bromonaphthyl)- β -6'-(1':2':3':4'-tetrahydronaphthyl)acrylic acid, m.p. 206—207°, cyclised to 5:6:7:8-tetrahydro-1:2-(1':2'-naphtha)-3-anthroic acid (III) (mainly), m.p. 238—243°, and 3:4-benz-5:6-tetramethylene-10-phenanthroic acid (IV), m.p. 286—287°. (III) and S at 270° for $\frac{1}{2}$ hr. afford 1:2-(1':2'-naphtha)-3-anthroic acid, m.p. 284—285°, decarboxylated to 1:2-(1':2'-naphth)-anthracene, m.p. 137—138° (dipicrate, m.p. 148—149°), which is purified through the anthraquinone, m.p. 273—274° ($\text{Na}_2\text{Cr}_2\text{O}_7\text{--AcOH}$). (IV) and S in $\text{C}_6\text{H}_5\text{N}$ at 240° for 3 hr. give 1:12-benzperylene-1'-carboxylic acid, m.p. 357—358°, decarboxylated to 1:12-benzperylene, m.p. 269—270° (picrate, new m.p. 266—267°) (cf. Clar, A., 1932, 731). A. T. P.

1:2:5:6-Dibenzphenanthrene. E. BERGMANN (J.C.S., 1938, 1291—1292; cf. preceding abstract and Weidlich, A., 1938, II, 314).—4-Keto-1:2:3:4-tetrahydrophenanthrene and $\text{Ph}[\text{CH}_2]_2\text{MgCl}$ afford 4- β -phenylethyl-1:2-dihydrophenanthrene, b.p. 180°/0.01 mm., cyclised by $\text{AlCl}_3\text{--CS}_2$ at 0° for 12 hr. to an oil, b.p. 190°/0.03 mm., which with Se at 325—330° for 24 hr. gives equal amounts of 1:2:5:6-dibenzphenanthrene, m.p. 128°, and a hydrocarbon, $\text{C}_{22}\text{H}_{18}$ (?), m.p. 98—100°. A. T. P.

Preparation of *m*-nitroaniline from *m*-dinitrobenzene.—See B., 1938, 1132.

Reductive alkylation of aniline. W. S. EMERSON and P. M. WALTERS (J. Amer. Chem. Soc., 1938, 60, 2023—2025).—Hydrogenation of NH_2Ph and RCHO in EtOH in presence of Raney Ni and a little NaOAc at room temp./3 atm. gives the stated yields of *N*-ethyl- (58%); picrate, m.p. 133—135°, -*n*-propyl- (52%), -*n*-butyl- (47%), -*n*-amyl- (62%); *m*-nitrobenzenesulphonyl derivative, m.p. 74—75°, -benzyl- (50%), and -*n*-heptyl-aniline, b.p. 125—130°/30 mm. (p-bromobenzenesulphonyl derivative, m.p. 115°); 10% of *tert*-amine is formed except with PhCHO and $\text{C}_6\text{H}_{13}\text{CHO}$, which give none. Some NH_2Ph is unchanged, indicating reversibility of the reactions. Other reaction conditions or use of Pt are less satisfactory. R. S. C.

Binary systems containing phenylenediamines.—See A., 1938, I, 575.

Analysis of technical β -naphthylamine-1-sulphonic acid.—See B., 1938, 1132.

Sulphanilamide derivatives. I. Aminoaryl-sulphonamidoaryl-sulphonic and -carboxylic acids. II. Disulphanilamides and related compounds. III. strepto-*N*-Polysulphanilylsulphanilamides and related compounds. M. L.

O** (A., II.)

CROSSLEY, E. H. NORTHEY, and M. E. HULTQUIST (J. Amer. Chem. Soc., 1938, 60, 2217—2222, 2222—2224, 2225—2227).—I. It is proposed to name sulphanilamide (I) derivatives by referring to the N of SO_2NH_2 as N^1 and the N of NH_2 as N^4 and by invariably naming $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2$ sulph-, met-, or orth-anilyl in complex derivatives. *p*- $\text{NHAcC}_6\text{H}_4\text{SO}_2\text{Cl}$ condenses with $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$ or $\text{NH}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ in H_2O at p_H 8—10, and the Ac of the products is removed by acid or base. Met- and orth-anilyl derivatives are prepared from $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$ and the NH_2 -acid, the product being reduced by $(\text{NH}_4)_2\text{S}_x$ or Fe in H_2O . The compounds marked * below are more active than (I) against β -haemolytic streptococci in mice. The following are described: Na sulphanilyl-sulphanilate (II), m.p. >300° (decomp.), 4-sulphanil-amido-2:5-dimethyl-, $+\text{H}_2\text{O}$, m.p. >300° (decomp.), 2:4-di(sulphanilamido)*, m.p. >320° (decomp.), and 3:4-di(sulphanilamido)-benzensulphonate, 4-sulphanilamidotoluene-3-, m.p. >300° (decomp.), and 2:4-di(sulphanilamido)toluene-5-sulphonate, m.p. >300° (decomp.); *N*-sulphanilyl-metanilic, m.p. >300° (decomp.), and -orthanilic*, m.p. >300° (decomp.), 5-sulphanilamidotoluene-2-, m.p. >300° (decomp.), 2-sulphanilamidotoluene-5-, m.p. >280° (decomp.), 4-sulphanilamidophenetole-2-, $+\text{H}_2\text{O}$, m.p. >245° (decomp.), 2:5-di(sulphanilamido)benzene* (III), $+\text{H}_2\text{O}$, m.p. >240° (decomp.), 4-amino-2-sulphanilamidobenzene-, $+0.5\text{H}_2\text{O}$, m.p. >270° (decomp.), sulphanil- β -naphthalide-6'-, m.p. >300° (decomp.), NN' -disulphanilbenzidide-2:2'-, m.p. >300° (decomp.), and 4:4'-di(sulphanilamido)stilbene-2:2'-disulphonic acid, $+4\text{H}_2\text{O}$, m.p. >330° (decomp.); Na sulphanil- α -naphthalide-4'-, $+0.5\text{H}_2\text{O}$, m.p. >245° (decomp.), and -5'-sulphonate, $+2\text{H}_2\text{O}$, m.p. >300° (decomp.); *p*-, m.p. 198—200.5°, *m*-, m.p. 197—198.5°, and *o*-sulphanilamidobenzoic acid*, m.p. 225° (decomp.), *o*-metanil-, m.p. 191.5—193.5°, and *o*-orthanil-amidobenzoic acid, m.p. 176.7—178°, and 5-sulphanilamidosalicylic acid, m.p. >285° (decomp.). (II) is ineffective against the common cold or influenza virus, but effective against dog distemper virus, whilst (III) is effective against the Francis strain of influenza virus in mice.

II. Adding 2.5 mols. of *p*- $\text{NHAcC}_6\text{H}_4\text{SO}_2\text{Cl}$ to aq. NH_3 at 10° and then keeping at p_H 10—12 (NaOH) and 35—40° gives Na N^4N^4 -diacetyldisulphanilamide [di-(*p*-acetamidobenzenesulphon)amide] (IV), hydrolysed by boiling 50% aq. NaOH to disulphanilamide, m.p. 260.5—261° [Na^+ , $+\text{H}_2\text{O}$, Mg , $+\text{H}_2\text{O}$, Li , Ca , Ba , Cu , Ni , Ag , Pb , Hg^{++} , Zn , NH_4 , NH_2Et , $\text{NH}_3\text{C}_5\text{H}_{11}$ (mixture), $\text{NH}_2(\text{C}_5\text{H}_{11})_2$, and $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_3$ salts]. With Me_2SO_4 in boiling xylene (IV) gives di-(*p*-acetamidobenzenesulphon)methylamide, m.p. 228.5—229°, cleaved by NaOH or, much faster, by boiling 20% aq. HCl to *p*- $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$ and *p*- $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NHMe}$, but hydrolysed to di-(*p*-aminobenzenesulphon)methylamide* (V), m.p. 180—181°, by dropping 36% HCl into its boiling solution in EtOH . Di-(*p*-acetamido-, m.p. 229.5—230.5°, and di-(*p*-amino-benzenesulphon)ethylamide* (VI), m.p. 153.3—154.7°, are similarly prepared. *m*- $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$ and *m*- $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$ in aq. $\text{NaOH--Na}_2\text{CO}_3$ at p_H 10—11 at 45—60° give Na di-*m*-nitrobenzenesulphonamide, reduced by $\text{NH}_3\text{--H}_2\text{S}$ to dimetanilamide,

m.p. $>300^\circ$ (decomp.). (V) and (VI) are effective against influenza virus in mice.

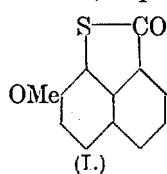
III. Compounds, $\text{NH}_2 \cdot [\text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH}]_x \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, containing only *p*-linkings, are given the prefix *strepto*. *p*-NHAc·C₆H₄·SO₂Cl with (I) or its derivatives at p_H 8–10 and subsequent hydrolysis give sulph-anilyl-*, m.p. 132·5–136°, and strepto-disulphanilylsulphanilamide*, m.p. 210·5–211·5°, Na strepto-disulphanilylsulphanilate, m.p. $>220^\circ$ (decomp.), strepto-trisulphanilylsulphanilic acid, $+2\text{H}_2\text{O}$, m.p. $>250^\circ$ (decomp.), *o*-N'-sulphanilylsulphanilamido-benzoic acid, m.p. 200–203°, sulphanilylsulphanil-*, m.p. 140–143°, and strepto-disulphanilylsulphanil- β -hydroxyethylamide, m.p. 137–143°, sulphanilylsulphanil-, m.p. 122·5–128°, and strepto-disulphanilylsulphanil-di-(β -hydroxyethyl)amide, m.p. 115·5–120·5°, sulphanilylsulphanil- β -hydroxypropyl-, m.p. 127·3–129·6°, and *N*-phenyl-*N*- β -hydroxyethyl-amide, m.p. 183–185°. Sulphanilylmetanilamide, $+0\cdot5\text{H}_2\text{O}$, m.p. 134–156°, *p*-toluenesulphonylsulphanildi-(β -hydroxyethyl)amide, m.p. 187–190°, Na N^N·di-metanilylsulphanilamide [metanil-*p*-metanilylsulphanilamide], m-NH₂·C₆H₄·SO₂·(*p*-NH·C₆H₄·SO₂·NNa·SO₂·C₆H₄·NH₂·m, m.p. 280° (decomp.), Na₂ disulphanilyldisulphanilamide, [*p*-NH₂·C₆H₄·SO₂·(*p*-NNa·C₆H₄·SO₂)₂NNa, m.p. 340° (decomp.), and sulphanilyldisulphanilamide, NH₂·C₆H₄·SO₂·NH·C₆H₄·SO₂·NH·SO₂·C₆H₄·NH₂, m.p. 198·5–206°, are similarly prepared. Metanilylsulphanilamide, m.p. 142–144°, is prepared by reduction (NH₃-H₂S) of *m*-NO₂·C₆H₄·SO₂·NH·C₆H₄·SO₂·NH₂·*p*. Metanilyl-metanil- β -hydroxyethylamide, m.p. 125–127·2°, and related compounds are obtained at p_H 7–9°.

R. S. C.

Chromatographic separation of *cis*- and *trans*-azobenzene. L. ZECHNEISTER, O. FREHDEN, and P. F. JÖRGENSEN (Naturwiss., 1938, 26, 495).—The mixture of *cis*- and *trans*-azobenzene obtained by exposure of the normal *trans*-form to sunlight (Hartley, A., 1938, II, 272) can be separated by the chromatographic method using a long tube filled with Al₂O₃ of a suitable type. C₆H₆ or benzine can be used as solvent and developer. The adsorption affinity of the *cis*-isomeride is considerably $>$ that of the *trans*-form.

A. J. M.

Synthesis of 2- and 6-substituted derivatives of 20-methylcholanthrene. L. F. FIESER and V. DESREUX (J. Amer. Chem. Soc., 1938, 60, 2255–2262).—2-Substituted cholanthrene derivatives are readily prepared by the Elbs reaction, but 6-substituted compounds are obtained, if at all, in very poor yield. Prep. of γ -keto- γ -*p*-anisylbutyric, m.p. 146·5–147°, γ -*p*-anisylbutyric, m.p. 60·5°, α -keto- δ -*p*-anisylvaleric, 7-methoxy-3 : 4-dihydro-1-naphthoic acid, m.p. 117·5°, and 7 : 1-OMe·C₁₀H₆·CO₂H, m.p.



169–170°, is described. The last and commercial SOCl₂ (probably containing SCl₂) give a compound, possibly (I), m.p. 143·5–144°, but with PCl₅ gives the acid chloride, m.p. 78·5°, which with the Li derivative from 7-chloro-4-methylhydrindene (modified prep.) yields 7-7'-methoxy-1'-naphthoyl-4-methyl-

hydrindene, m.p. 91·4–91·6°, converted at 405–420° alone (40%) or in presence of Zn dust (36% yield) into 2-methoxy-20-methylcholanthrene, dimorphic, m.p. 163–163·4° (picrate, m.p. 185·5–186°). This product is resistant to hydrolysis and the derived OH-compound is sensitive to reagents; however, with AcOH-HBr in N₂ at 140°, followed by Ac₂O-NaOAc in N₂, it yields 2-acetoxy-, m.p. 218–219° (sealed tube), decomp. $\sim 210^\circ$ (open tube), and thence by aq. EtOH-NaOH at 40° in N₂ 2-hydroxy-20-methylcholanthrene, m.p. 225·5–226° (picrate, m.p. 204°). 7-4'-Methoxy-1'-naphthoyl-4-methylhydrindene, m.p. 121·5–122°, is obtained from 7-cyano-4-methylhydrindene (II) and 1 : 4-OMe·C₁₀H₆·MgBr or from 4-methylhydrindene-7-carboxyl chloride (III), α -C₁₀H₇·OMe, and AlCl₃ in C₂H₂Cl₄ at 0°; at 405° it gives only methylcholanthrene (IV). Prep. of the starting materials for these syntheses is modified. 4 : 1-C₁₀H₆Br·NHAc (prep. by Br in AcOH at 10°) gives the amine, which yields (diazo-reaction) 1 : 4-C₁₀H₆ClBr, also obtained in very poor yield from 1-C₁₀H₇Cl and Br in CCl₄. 4 : 1-C₁₀H₆Cl·MgBr and (II) give 7-4'-chloro-1'-naphthoyl-4-methylhydrindene (V), m.p. 144·5–145°, which by the Elbs reaction yields 1·2% of 6-chloro-20-methylcholanthrene (VI), m.p. 233·5–233·8° (vac.), and much (IV). CuCN, (VI), and a trace of MeCN in C₅H₅N at 230–240° yield smoothly 6-cyano-20-methylcholanthrene, m.p. 268–268·5° (vac.), which resists hydrolysis. 1-C₁₀H₇Cl, (III), and AlCl₃ alone do not react, but in C₂H₂Cl₄ a substance, m.p. 215°, probably 4-chloro-10-methyl-8 : 9-trimethylenebenzanthrone-7, is formed. This substance is obtained also from (V) by AlCl₃ in C₂H₂Cl₄; it is unaffected by Ac₂O-C₅H₅N, but gives an unstable dihydroenol acetate by Zn dust-NaOAc-Ac₂O. 1-C₁₀H₇Cl is isomerised to 2-C₁₀H₇Cl by AlCl₃ in C₂H₂Cl₄. M.p. are corr.

R. S. C.

Oxidation processes. XII. Autoxidation of quinol and of the mono-, di-, and tri-methylquinols. T. H. JAMES, J. M. SNELL, and A. WEISSBERGER (J. Amer. Chem. Soc., 1938, 60, 2084–2093; cf. A., 1938, II, 96).—The relative rates of autoxidation of *p*-C₆H₄(OH)₂ (I) in H₂O, tolu- (II), *o*-, *m*-, and *p*-xylo- (III), ψ -curo- (IV), and duro-quinol (V) in 20% EtOH are 1·0, 3·9, 10·5, 18·2, 17·0, 31·0, and 1·0 (uncatalysed), respectively. The primary products are the quinone and H₂O₂, but later oxidation of all except duroquinone to hydroxyquinones occurs. The formation of *p*-benzoquinone and hydroxy-*p*-benzoquinone is confirmed by reaction with 1-methylbenzothiazole metho-*p*-toluenesulphonate to give compounds having absorption max. at 6200 (min. at 4200–4600) and 4500–4600 (min. at 5400–5500; slight max. at 6200–6300) Å., respectively. The oxidations are reactions of the first order. That of (IV) has a short induction period, removed by adding the quinone, which thus has a catalytic effect; in this respect (IV) is intermediate between (V) and (I)–(III). Possibly oxidation of (I)–(III) is catalysed by such small amounts of quinone that all the reactions observed are in fact fully catalysed. In the range p_H 7·2–8·2 the rate of oxidation is $\propto [\text{OH}]^2$ and thus the concn. of the doubly charged quinol ion, which confirms the view that the rate is

determined by the formation of the semiquinone. Dependence of the rate of oxidation of (IV) on the $[O_2]$ increases as the concn. of quinone and the rate finally becomes almost $\propto [O_2]$. p -OH·C₆H₄·OMe and duroquinol Me ether are very slowly oxidised, quinone being without effect on this reaction. Except for (V), Na₂SO₃ inhibits the autoxidations. R. S. C.

Azo-dyes from thiol- and methylthiol- β -naphthols. E. JUSA and B. HÖNIGSFELD (Monatsh., 1938, 72, 93—114; cf. A., 1934, 1097).—O-Carbethoxy- β -naphthol-5-sulphonyl chloride (Pollak *et al.*, A., 1929, 1441) and Zn-HCl-EtOH give 5-thiol-O-carbethoxy- β -naphthol (I), m.p. 50° [S-picryl derivative, m.p. 178° (also +C₆H₆)], which with Me₂SO₄-Na₂CO₃-Et₂O affords the Me thioether (II), m.p. 64°, converted by excess of Me₂SO₄ for 2 weeks at room temp. into 5-methylthiol-2-methoxynaphthalene, m.p. 71°. (I) and (II) and aq. KOH-EtOH at b.p. afford 5-thiol- β -naphthol (III), m.p. 82° (S-picryl, m.p. 185—190°, and OS-Bz₂ derivative, m.p. 200°), and 5-methylthiol- β -naphthol (IV), m.p. 55·5°, respectively. (I) and (III) and aq. FeCl₃-EtOH yield bis-(O-carbethoxy- β -naphthol), m.p. 120°, and bis-(β -naphthol), m.p. 197°, 5:5'-disulphide, respectively. (III) and CH₂Cl·CO₂K (V) in aq. KOH and N₂ form β -naphthol-5-thioglycollic acid, m.p. 109°, but excess of (V) gives 2-carboxymethoxynaphthalene-5-thioglycollic acid, m.p. 201°. (III) and (IV), coupled with p -NO₂·C₆H₄·N₂Cl (in N₂), give 1- p -nitrobenzeneazo-5-thiol- (orange-red) and -5-methylthiol- (bluish-red) - β -naphthol, respectively. Similarly O-carbethoxy- β -naphthol-4-sulphonyl chloride, m.p. 117°, gives 4-thiol-O-carbethoxy- β -naphthol (picryl derivative, m.p. 153°), and thence its Me thioether, β -naphthol-4-thioglycollic acid, 4-thiol- and 4-methylthiol- β -naphthol, and 1- p -nitrobenzeneazo-4-thiol- (orange-red) and -4-methylthiol- (orange) - β -naphthol.

O-Carbethoxy- β -naphthol-1-sulphonyl chloride, m.p. 117° [whence the sulphanilide, m.p. 129°, hydrolysed (KOH-EtOH) to β -naphthol-1-sulphanilide, m.p. 183°], with Zn-HCl-EtOH afford 2-naphthylene-1-thiol-carbonate (VI), m.p. 107° (cf. Stevenson and Smiles, A., 1930, 1285), converted by KOH-EtOH (in N₂) into 1-thiol- β -naphthol (VII) [Bz₂ derivative, m.p. 166°; bis-(β -naphthol) 1:1'-disulphide, m.p. 169° (Bz₂ derivative, m.p. 191·5°)]. (VI) or (VII) with (V) gives β -naphthol-1-thioglycollic acid, m.p. 113°, and with Me₂SO₄-Na₂CO₃-KOH affords 1-methylthiol-2-methoxynaphthalene, b.p. 260°/12 mm. (slight decomp.), and (?) 2-hydroxy-2'-methoxy-1:1'-dinaphthyl disulphide. Cotton impregnated with (VII) and developed with p -NO₂·C₆H₄·N₂Cl (VIII) is dyed a dull reddish-orange, but coupling in substance affords a product containing approx. one third of the calc. amount of N. Derivatives of 2:1-OH·C₁₀H₆·SO₃H, e.g., the K salt, sulphanilide, 1-thioglycollic acid, with (VIII) give unstable azo-ethers (?) of variable N content. A. T. P.

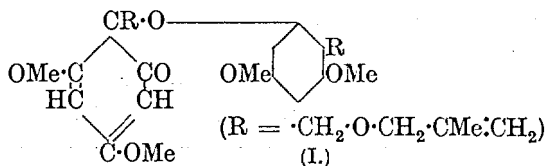
Manufacture of 4-nitro-2-amino-1-naphthol-sulphonic acids.—See B., 1938, 1135.

Carboxylic esters of chaulmoogryl and hydnocarpyl alcohols. K. BURSCHKIES (Ber., 1938, 71, [B], 1855—1859).—Hydnocarpyl alcohol and crotonic

anhydride under N₂ at 100° give *hydnocarpyl crotonate*, b.p. 180°/0·3 mm. The following *chaulmoogryl* esters are obtained by heating the alcohol with the requisite acid chloride in a current of an inert gas: *tiglate*, b.p. 190—192°/0·05 mm.; *palmitate*, b.p. 260—262°/0·02 mm., m.p. 45—46°; *stearate*, b.p. 260°/0·05 mm., m.p. 51°; *oleate*, b.p. 268—270°/0·1 mm. Heating the acid with the alcohol under atm. or reduced pressure in an inert gas at a high temp. leads to the following esters: *chaulmoogryl ricinoleate*, b.p. 230—250°/0·01 mm., *p*-bromocinnamate, b.p. 252—256°/0·2 mm., and *p*-cumenylacrylate, b.p. 245—250°/0·1 mm.; *hydnocarpyl linoleate*, b.p. 240—250°/0·01 mm., and *p*-methoxycinnamate, b.p. 230—238°/0·1 mm. A mixture, b.p. 192—196°/0·1 mm., of chaulmoogryl and hydnocarpyl cinnamates is prepared. The esters appear to afford an improved treatment of leprosy. H. W.

[Picrato]diammines of bivalent platinum.—See A., 1938, I, 581.

Bæckeol. A. R. PENFOLD and J. L. SIMONSEN (J. Proc. Roy. Soc. New South Wales, 1938, 71, 291—296).—The ether, m.p. 103—104° (acetate, m.p. 71—72°), previously (Penfold and Morrison, B., 1924, 576) isolated from, e.g., *Bæckeia crenulata*, is now termed *bæckeol* and shown to be probably 2- β -methylallyloxymethylphloroglucinol 3:5-Me₂ ether. It is readily sol. in hot, but sparingly in cold, alkali, is indifferent to Zn dust and alkali, gives red amorphous products with HBr or HI, with Br-AcOH gives an unstable cryst. bromide, with NaOEt at 200—220° in N₂ gives 1:2:4:6-C₆H₂Me(OMe)₂·OH, with NaOMe-MeOH at 250° in N₂ gives 1:3:5:2:4-C₆HMe₃(OH)₂, and with H₂O₂-KOH-MeOH gives Pr⁶⁰CO₂H. With O₃ it gives only traces of CH₂O and unidentifiable products. Its oily Me ether, obtained from the K salt by an excess of Me₂SO₄ (not by CH₂N₂), is converted by KMnO₄ into (?) 2- β -keto-n-propoxy-methylphloroglucinol Me₃ ether, m.p. 65—66°, and a gummy acid (oxidised by dil. HNO₃ to H₂C₂O₄), by HNO₃ (d 1·4) into (?) 4-nitro-2- β -nitro-n-propoxy-methylphloroglucinol Me₃ ether, m.p. 115—116°, and by hot, dil. HNO₃ into H₂C₂O₄. It absorbs 6 (cold) and 6·7 (hot) H₂ catalytically, which implies reduction of the Ph ring, the OH, and two of the ethereal O. With K₃Fe(CN)₆-KOH it gives an oxide [? (I)],



C₂₆H₃₄O₈, anhyd., m.p. 127—128°, or, air-dried, double m.p. 97° and 127°. HNO₃-H₂SO₄ replaces a OMe and gives 5-nitro-2- or -6- β -methylallyloxy-resorcinol 3-Me ether, m.p. 106°. R. S. C.

Replaceability of aromatically united hydrogen by lithium by means of lithium phenyl. G. WITTIG, U. PÖCKELS, and H. DRÖGE (Ber., 1938, 71, [B], 1903—1912).—Li and p -C₆H₄Br·OMe in Et₂O and N₂ give p -bromo-*o*-lithioanisole (I), transformed by CPh₃ into 32·5% of 5-bromo-2-methoxy-

triphenylcarbinol (II), m.p. 127—128°; PhOMe, *p*-C₆H₄Br·OMe, dianisyl, and diphenyl-*p*-anisylcarbinol are obtained as by-products. (II) is converted by boiling HCl-EtOH or HI-AcOH into 5-bromo-2-methoxytriphenylmethane, m.p. 133°, transformed by distillation with Zn dust (vac.) into *o*-OMe-C₆H₄·CHPh₂, m.p. 114°. *o*-Methoxytriphenylcarbinol and Br in AcOH afford (II). The yield of organometallic derivative supports the view that its formation is not due to immediate replacement of H *ortho* to OMe by Li but that *p*-C₆H₄Li·OMe (A) is formed and then reacts, (A) + C₆H₄Br·OMe → Li·C₆H₃Br·OMe + PhOMe. The probability that other organolithium compounds can convert *p*-C₆H₄Br·OMe into (I) is established as follows. LiPh and *p*-C₆H₄Br·OMe are allowed to react in Et₂O for 24 hr. and then treated with CPh₃·OH, thus giving CPh₃·OH and (II) (yield 70%). PhOMe and LiPh at room temp. do not appear to react but the product formed at 100° is transformed by CPh₃·OH into *o*-methoxytriphenylcarbinol, m.p. 129—129.8°; if CPh₃·OH is added to the cold mixture the products are CPh₃·OH and a colourless, unidentified hydrocarbon, m.p. 220—221°. LiPh and *p*-C₆H₄(OMe)₂ when treated with CPh₃·OH after many hr. contact give 2:5-dimethoxytriphenylcarbinol, m.p. 142—143.2° (yield 65%) with about 12% of CPh₃·OH, whereas after short contact the product is mainly CPh₃·OH. Similarly after 60 hr. the Li compound separates from LiPh and *m*-C₆H₄(OMe)₂ in Et₂O; it is transformed by CPh₃·OH into 2:4-dimethoxytriphenylcarbinol, m.p. 134.5—136° (yield 72%); after 5 hr. at 15—20° this compound and CPh₃·OH are isolated. 4:6:1:3-C₆H₂Br₂(OMe)₂ (III) and LiPh rapidly yield PhBr and 4-bromo-6-lithio-1:3-dimethoxybenzene, the constitution of which is determined by its transformation by CO₂ into 2:4:5:1-(OMe)₂C₆H₂Br·CO₂H (IV), m.p. 194.5—195.5°, and by CPh₃·OH into 5-bromo-2:4-dimethoxytriphenylcarbinol, new m.p. 192.8—193.8°. Tri-(5-bromo-2:4-dimethoxyphenyl)carbinol, m.p. 240°, and di-(5-bromo-2:4-dimethoxyphenyl) ketone, m.p. 225—227°, are obtained as by-products of the prep. of (IV). 4-Bromo-1:3-dimethoxybenzene has m.p. 24—26°. MgPhBr appears without action on *p*-C₆H₄Br·OMe and (III) at 100°/16 hr. H. W.

High-vacuum distillation of materials containing sterols and related compounds.—See B., 1938, 1231.

Oestradiol 3-*n*-valerate, m.p. 58—60°, -hexoate, m.p. 46—51°, -octoate, m.p. 48—53°, and -decoate, m.p. 59—60°, and 17-*n*-hexoate, m.p. 128.5—129°, and -octoate, m.p. 117.5—118°.—See A., 1938, III, 807.

Constitution of the "pregnanetriol" occurring in the urine of pregnant mares. A. D. ODELL and G. F. MARRIAN (J. Biol. Chem., 1938, 125, 333—340).—The triacetate of the triol, C₂₁H₃₆O₃ (I) (Haslewood *et al.*, A., 1934, 1126) [= Marker's pregnanetriol-*B* (A., 1938, II, 97)], when hydrolysed even by 0.8 mol. of KOH in MeOH, gives the triol monoacetate, C₂₁H₃₆O₂·OAc, m.p. 222—224°, oxidised by CrO₃ in 90% AcOH to the diketolalcohol

monoacetate (II), m.p. 191—192° (pyridazine derivative, decomp. from 210°, m.p. >310°), the *disemicarbazone*, slight decomp. 220—223°, m.p. >305°, of which with EtOH-NaOEt at 168—170° gives the alcohol (III), C₂₁H₃₆O, m.p. 82—83° (benzoate, m.p. 141°). Pb(OAc)₄ at room temp. or 37° is without effect on (I); which is thus not an αβ-diol. (I) may be pregnane- or allopregnane-3(α):6:20-triol. Marker's ketodiol diacetate, m.p. 188° (A., 1938, II, 277), may be (II), and the reduction product, believed to be allopregnane, may be (III) (? allopregnan-20-ol). R. S. C.

Reformatsky condensations involving vinyl-ogues of haloacetic esters. R. C. FUSON, R. T. ARNOLD, and H. G. COOKE, jun. (J. Amer. Chem. Soc., 1938, 60, 2272—2273).—CH₂I·CH·CH·CO₂Et, PhCHO, and Zn in Bu₂O give an impure OH-ester, b.p. 162—165°/4 mm. [with PhNCO gives CO(NHPh)₂; with Na₂Cr₂O₇-H₂SO₄ gives BzOH], converted by KOH-EtOH into Ph·[CH·CH]₂·CO₂H. *p*-C₆H₄Cl·CHO also gives a partly dehydrated ester, converted by KOH into δ-*p*-chlorophenyl-Δ^α-penta-dienoic acid, m.p. 251° (decomp.; corr.) [Me ester, m.p. 132° (corr.)], also obtained from *p*-C₆H₄Cl·CH·CH·CHO, CH₂(CO₂H)₂, and a little piperidine in boiling C₆H₅N. cycloHexanone gives *Et* δ-cyclohexyl-Δ^α-penta-dienoate, b.p. 143—148°/8 mm. *Et* γ-iodobutyrate (prep. from the Cl-ester), b.p. 84—85°/4 mm., reacts very slowly with *p*-C₆H₄Cl·CHO and gives only a minute yield of *Et* δ-*p*-chlorophenyl-pentaenoate, m.p. 122—123°. R. S. C.

Conversion of quinic acid into shikimic acid. G. DANGSCHAT and H. O. L. FISCHER (Naturwiss., 1938, 26, 562—563; cf. A., 1937, II, 382).—3-Acetyl-4:5-methylenequinamide, m.p. 149°, with *p*-C₆H₄Me·SO₂Cl and C₅H₅N yields the nitrile, b.p. 128°/0.2 mm., of 3-acetyl-4:5-methyleneshikimic acid, which in turn gives methyleneshikimic, m.p. 138°, and shikimic acid. Hence C₍₃₎, C₍₄₎, and C₍₅₎ of quinic acid have the same configuration as those of *d*-glucose. A. Lr.

New diene syntheses. IV. E. LEHMANN (Ber., 1938, 71, [B], 1874—1878; cf. A., 1935, 978; 1936, 605).—β-Phenyl-Δ^β-penta-diene (I) and CH₂·CH·CO₂H in C₆H₆ at 100—105° afford 2-phenyl-2-methyl-Δ³-tetrahydrobenzoic acid, two forms, m.p. 142° and 138°. Similarly β-*p*-tolylpenta-diene (II) yields 2-*p*-tolyl-2-methyl-Δ³-tetrahydrobenzoic acid, forms, m.p. 204° and 181—182° (III); KOH-EtOH transforms 2-*p*-tolyl-2-methyl-Δ³-tetrahydrobenzaldehyde (IV) into (III) and a variety m.p. 174°, together with 2-*p*-tolyl-2-methyl-Δ³-tetrahydrobenzyl alcohol, b.p. 194—197°/13 mm., m.p. 84°, also obtained by reduction (Na-Hg, aq. MeOH) of (IV). β-*m*-Xylylpenta-diene and CH₂·CH·CO₂H give 2-*m*-xylyl-2-methyl-Δ³-tetrahydrobenzoic acid, forms, m.p. 147° and 139—140°. Maleic anhydride and (I) in C₆H₆ at 100—105° give 3-phenyl-3-methyl-Δ⁴-tetrahydrophthalic acid, m.p. 178°; the 3-*p*-tolyl-, m.p. 185—186° or 178° after keeping, and 3-*m*-xylyl-, m.p. 184°, derivatives are obtained similarly. *p*-Benzoquinone with (I) and (II) in C₆H₆ at 105° gives 1:8-diphenyl-1:4:5:8-diendomethyl-ene-1:4:5:8-tetrahydroanthraquinone, m.p. 233°,

and the corresponding 1 : 8-*di-p-tolyl* derivative, m.p. 256°; simultaneous occurrence of dehydrogenation is proved by the formation of quinol and quinhydrone.

H. W.

Chemotherapeutic studies in the acridine series. VI. F. R. BRADBURY and W. H. LINNELL (Quart. J. Pharm., 1938, 11, 240—251).—See A., 1938, III, 938. The following are described: 4-nitro-4'-acetamidodiphenylamine-2-carboxylic acid, m.p. 285° (decomp.); Me 5-nitro-, m.p. 101—102°, and 5-amino-diphenylamine-2-carboxylate, m.p. 71—72° (hydrochloride, m.p. 186—187°; Ac derivative, m.p. 174—176°). 1 : 2 : 4-C₆H₃MeCl·NO₂ can be obtained in 90% yield by chlorinating *p*-C₆H₄Me·NO₂ at 60—70° in presence of SbCl₃. Attempts to synthesise 3-amino-5 : 5-dimethyl- and -diphenyl-5 : 10-dihydroacridine were unsuccessful.

J. N. A.

Preparation of amyl salicylates. A. F. FREEMAN and H. L. HALLER (J. Amer. Chem. Soc., 1938, 60, 2274—2275).—*n*-Amyl salicylate, b.p. 116—121°/1.4 mm., is prepared from the alcohol and acid by H₂SO₄. *CHMePr*^a, b.p. 107—110°/4—5 mm., and *CM₂Et* salicylate, b.p. 84—86°/3 mm., are obtained from the alcohol, *o*-OH·C₆H₄·COCl, and a little AlCl₃, but not from the acid and H₂SO₄. R. S. C.

Aminoalkyl esters of *p*-hydroxybenzoic and anisic acids.—See B., 1938, 1135.

Formation of an acid anhydride by the action of water on organometallic complexes. W. F. BRUCE (J. Amer. Chem. Soc., 1938, 60, 2277).—The Grignard reagent from 4-bromo-7-isopropylhydrindene and α -C₁₀H₇·COCl (I) in Et₂O give 50% of 4- α -naphthoyl-7-isopropylhydrindene, b.p. 225—235°/1.2 mm., 28% of 4-isopropylhydrindene, b.p. 88—90°/1 mm., and 22% of (α -C₁₀H₇·CO)₂O (II). Dissolution of Li in a solution of 4-bromo-2 : 7-dimethylhydrindene in Et₂O and addition to (I) gives a transient red colour (not due to Fe) and yields much (II) and α -C₁₀H₇·CO₂H with less 2 : 4-dimethylhydrindene, b.p. 100—105°/23 mm., and a trace of (?) 4- α -naphthoyl-2 : 7-dimethylhydrindene, b.p. 200—235°/4 mm. R. S. C.

1-Hydroxy-2-naphthoyl derivatives of aromatic diamines.—See B., 1938, 1135.

Fluorencarboxylic acids and ethylanilides.—See B., 1938, 1134.

***o*-Anisylmalonic acid and its derivatives.** J. B. NIEDERL and R. T. ROTH (J. Amer. Chem. Soc., 1938, 60, 2140—2141).—*o*-OMe·C₆H₄·CH₂Cl (prep. from the alcohol and HCl at <20°) and NaCN in hot aq. EtOH give *o*-OMe·C₆H₄·CH₂·CN (I) and *o*-OMe·C₆H₄·CH₂·OEt. With Et₂CO₃ and Na in Et₂O (I) gives *Et o-anisylcyanoacetate* (II), m.p. 49°, hydrolysed by 2% NaOH to *o-anisylmalonic acid* (III), m.p. 142—143°, and by conc. NH₃ to *o-anisylcyanoacetamide*, m.p. 142—143°. With HCl-EtOH (II) gives the *Et₂* (IV), b.p. 133—135°/2 mm., and *Et H* ester, m.p. 86—87°, of (III), both hydrolysed by NaOH to (III), which at 150° gives CO₂ and *o*-OMe·C₆H₄·CH₂·CO₂H. With aq. NH₃ (IV) gives the *diamide*, m.p. 204°. R. S. C.

Diels-Alder reaction between naphthylcyclopentenes and maleic anhydride. W. E. BACH-

MANN and M. C. KLOETZEL (J. Amer. Chem. Soc., 1938, 60, 2204—2210).—Contrary to Bergmann and Bergmann (A., 1937, II, 407), 1- α - or - β -naphthyl- Δ^1 -cyclopentenes add (CH·CO)₂O (I) in hot xylene or, better, when fused without a solvent. The adducts are hydrolysed and the Ca salts of the resulting acids are heated with CaO + Zn dust; good yields of aromatic hydrocarbons result, unless OMe or angular Me is present, in which case only oils are obtained. 1-C₁₀H₇·CH·CH₂ (II) and (I) give 1 : 2 : 3 : 10a-tetrahydrophenanthrene-1 : 2-dicarboxylic acid (with the anhydride), the Ca salt of which with CaO gives phenanthrene (III). The adduct and S at 255° give phenanthrene-1 : 2-dicarboxylic anhydride (IV) (*Et₂* ester, m.p. 132°, of the corresponding acid), the Ca salt from which with CaO and Zn dust gives (III). *Et H* maleate and (II) at 100° give *Et* (1 or 2) *H* (2 or 1) 1 : 2 : 3 : 10a-tetrahydrophenanthrene-1 : 2-dicarboxylate, converted by S at 250—260° into (IV) and by basic Cu carbonate in quinoline into a substance, m.p. 246—247°. 1-C₁₀H₇·MgBr and cyclopentanone give 1- α -naphthylcyclopentan-1-ol, m.p. 75.5—76°, dehydrated by KHSO₄ or HCO₂H to 1- α -naphthyl- Δ^1 -cyclopentene, cryst. (picrate, m.p. 79—80°), which with (I) gives 3 : 4-cyclopentano-1 : 2 : 3 : 10a-tetrahydrophenanthrene-1 : 2-dicarboxylic acid (V), m.p. 211—213° (decomp.), and its anhydride. The acid with S at 230—240° in CO₂ gives 3 : 4-trimethylenephenanthrene-1 : 2-dicarboxylic anhydride, m.p. 321°, which with basic Cu carbonate in quinoline gives 3 : 4-trimethylenephenanthrene, m.p. 71—72° (picrate, m.p. 134—135°), also obtained from the Ca salt of (V) by distilling it with CaO and Zn dust. 2-Methylcyclopentanone and 1-C₁₀H₇·MgBr lead similarly to 1- α -naphthyl-2-methyl- Δ^1 -cyclopentene (not obtained pure), b.p. 165—168°/1 mm., and 3-methyl-3 : 4-cyclopentano-1 : 2 : 3 : 10a-tetrahydrophenanthrene-1 : 2-dicarboxylic acid, a gum. 2-C₁₀H₇·MgBr gives similarly 1- β -naphthyl-, m.p. 85—86°, and 1- β -naphthyl-2-methyl- Δ^1 -cyclopentene, an oil, 1 : 2-cyclopentano- and 2-methyl-1 : 2-cyclopentano-2 : 3 : 4 : 4a-tetrahydrophenanthrene-3 : 4-dicarboxylic acid, solids, and 1 : 2-trimethylenephenanthrene, m.p. 135—136° (picrate, m.p. 130—132°). 6 : 2-OMe·C₁₀H₆·MgBr leads to 1-6'-methoxy-2'-naphthyl-, m.p. 141—142° (lit. 148°), and 1-6'-methoxy-2'-naphthyl-2-methyl- Δ^1 -cyclopentene, m.p. 74—75°, 7-methoxy-1 : 2-cyclopentano-, m.p. 310° (decomp. from 280°), and 7-methoxy-2-methyl-1 : 2-cyclopentano-2 : 3 : 4 : 4a-tetrahydrophenanthrene-3 : 4-dicarboxylic acid, m.p. 292° (decomp. from 275°). The 1 : 2 : 3 : 10a- and 2 : 3 : 4 : 4a-tetrahydrophenanthrene derivatives may be 1 : 2 : 3 : 4-H₄-compounds. R. S. C.

Determination of cholic acid. II. Improved Gregory-Pascoe method. T. SHIMADA (J. Biochem. Japan, 1938, 28, 149—160; cf. A., 1938, II, 364).—The application of the furfuraldehyde-H₂SO₄ reaction (A., 1929, 1114) to the determination of cholic acid is described and exemplified. F. O. H.

Catalytic reduction of chaulmoogroyl chloride according to Rosenmund. T. WAGNER-JAUREGG and R. VOIGT (Ber., 1938, 71, [B], 1973—1980).—The mixed fatty acids from chaulmoogra oil ("hydno-

chaulic acid"), b.p. 180—190°/0.1 mm., $[\alpha]_D +51.8^\circ$, with SOCl_2 in N_2 give *hydnochaulyl chloride*, b.p. 165—175°/0.1 mm., $[\alpha]_D +48.8^\circ$, transformed by H_2 in boiling xylene containing $\text{Pd}-\text{BaSO}_4$ and quinoline-*S* into optically active *hydnochaulaldehyde*, b.p. 140—150°/0.1 mm., $[\alpha]_D +15.67^\circ$. In presence of Rosenmund's catalyst the chloride yields mainly *isohydnochaulaldehyde* (I), b.p. 138—140°/0.05 mm., $[\alpha]_D \pm 0^\circ$ [2 : 4-dinitrophenylhydrazones, m.p. 85—88°; *semicarbazone*, m.p. 98—100°; *oxime*, m.p. 83—86°; $(\text{CH}_2\text{Ph})_2$ *acetal*, b.p. 220—240°/0.1 mm.], reduced (H_2 , PtO_2 , AcOH) to dihydrohydnochaulaldehyde, b.p. 145—155°/0.1 mm. (2 : 4-dinitrophenylhydrazones, m.p. 102—104°). Treatment of (I) with PCl_3 at -15° and then at 5° to 8° and of the product with H_2O , NaOH , and finally with $\text{Ba}(\text{OAc})_2$ gives the salt, $\text{C}_{18}\text{H}_{33}\text{O}_4\text{PBA}$ (corresponding Na salt). Analogously $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ gives α -hydroxycinnamylphosphonic acid, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{PO}(\text{OH})_2$, isolated as the *Ba* (+ $2\text{H}_2\text{O}$) and *Na* (+ $2\text{H}_2\text{O}$) salts. Chaulmoogroyl chloride, $[\alpha]_D +56.3^\circ$, is reduced to *isochaulmoograldehyde*, which is oxidised (Ag_2O) to *isochaulmoogric acid*. H. W.

Reaction of acid anhydrides with anils. H. R. SNYDER, R. H. LEVIN, and P. F. WILEY (J. Amer. Chem. Soc., 1938, 60, 2025—2027).— $(\text{CHPh}\cdot\text{N})_2$ (I) and $(\text{CH}\cdot\text{CO})_2\text{O}$ (II) in moist Et_2O give PhCHO and 78% of *maleinmono(benzylidenehydrazide)* (III), $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, m.p. 183°. In the absence of H_2O only a trace of (III) is formed, so that reaction proceeds thus: $(\text{I}) + \text{H}_2\text{O} \rightleftharpoons \text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{OH} \rightleftharpoons \text{PhCHO} + \text{CHPh}\cdot\text{N}\cdot\text{NH}_2$ (IV); $(\text{IV}) + (\text{II}) \rightarrow (\text{III})$. In hot H_2O (III) yields maleic acid, N_2H_4 , and (I). Conversion of $\text{NPh}\cdot\text{CHPh}$ by Ac_2O at 55—65° into $\text{NAcPh}\cdot\text{CHPh}\cdot\text{OAc}$ is hastened by adding a little AcOH ; the first step is thus addition of AcOH to give $\text{NHPh}\cdot\text{CHPh}\cdot\text{OAc}$. $\text{Ac}_2\text{O}-\text{AcOH}$ does not convert (I) into $\text{CHPh}\cdot\text{N}\cdot\text{NAc}\cdot\text{CHPh}\cdot\text{OAc}$ at 55—65° (cf. Ekeley *et al.*, A., 1936, 740) and at 100° gives $(\text{NHAc})_2$ and $\text{CHPh}\cdot\text{N}\cdot\text{NHAc}$. Products obtained from anils by AcOH and AcSH and previously formulated as $\cdot\text{NAc}\cdot\text{CH}(\text{OH})\cdot$ and $\cdot\text{NAc}\cdot\text{CH}(\text{SH})\cdot$ are considered to be $\cdot\text{NH}\cdot\text{CH}(\text{OAc})\cdot$ and $\cdot\text{NH}\cdot\text{CH}(\text{SAC})\cdot$, respectively.

Formation of $o\text{-C}_6\text{H}_4\langle\text{CO}\cdot\text{O}\rangle_{\text{NAc}}\text{CHPh}$ from $o\text{-CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (V) and Ac_2O occurs by intramol. ring-closure; PhNCO gives 6-keto-3-phenyl-carbamyl-2-phenyl-3 : 6-dihydro-4 : 5-benz-1 : 3-oxazine, $o\text{-C}_6\text{H}_4\langle\text{CO}\cdot\text{O}\rangle_{\text{N}(\text{CO}\cdot\text{NHPh})}\text{CHPh}$, m.p. 171°, hydrolysed by hot, dil. HCl to PhCHO and $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$. No reaction occurs between (V) and (II), $(\text{CH}_2\cdot\text{CO})_2\text{O}$, or $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ alone or in hot dioxan or C_6H_6 , but in C_6H_6 in moist air $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NHR}$ ($\text{R} = \text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ or $\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$) is formed. In CCl_4 (V) exists partly, and $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CHPh}$ wholly, in the dicyclic form (infra-red absorption). R. S. C.

Benzoin reaction. VI. Effect of temperature variation on the benzoin reaction. B. F. FERREIRA and T. S. WHEELER (Proc. Indian Acad. Sci., 1938, 8, A, 61—64; cf. A., 1936, 471).—A study of the reaction at various temp. shows that between 80° and

110° the rate of the fast homogeneous reaction in absence of solvent or diluent remains const., but that of the slow heterogeneous reaction is approx. doubled for each 10° rise. Some decomp. of the benzoin occurs at $>110^\circ$. A. Li.

Condensation of acyclic aldehydes with cyclanic ketones. Condensation of formaldehyde and acetaldehyde with *cyclohexanone*. H. GAULT and E. STECKL (Compt. rend., 1938, 207, 475—477; cf. A., 1938, II, 411).—*cycloHexanone* (I) (2 mols.) with CH_2O (1 mol.) and $\text{Ca}(\text{OH})_2$ affords 2 : 2-di-(hydroxymethyl)cyclohexanone, b.p. 170—171°/15 mm., m.p. 52—53° (*phenylhydrazones*, m.p. 131—132°; *Ac derivative*, b.p. 180°/15 mm.), and 2-hydroxymethylcyclohexanone (II) (major product); K_2CO_3 instead of $\text{Ca}(\text{OH})_2$ favours the formation of the former. In certain experiments a compound, $\text{C}_{11}\text{H}_{20}\text{O}_2$ (? $\text{C}_9\text{H}_{12}\text{O}_2$), m.p. 155°, which may arise by addition of $3\text{CH}_2\text{O}$ to (I) and elimination of $2\text{H}_2\text{O}$, is isolated. (II) in EtOH with H_2 -Raney Ni at room temp. affords 2-hydroxymethylcyclohexanol (cf. A., 1932, 1126) (*monophenylcarbamate*, m.p. 145°; *Ac*, b.p. 128°/13 mm., and *Bz*, b.p. 120°/1 mm., derivatives). As above, (I) with MeCHO affords 2- α -hydroxyethylcyclohexanone, b.p. 89—90°/3 mm., 2-ethylidenecyclohexanone, and other products. (II) is better prepared from (I) and 12% CH_2O (cf. Mannich and Brose, A., 1923, i, 565). J. L. D.

Reactions of γ -ketonic acids. V. Ketonic β -lactones and the Walden inversion. E. P. KOHLER and J. E. JANSEN (J. Amer. Chem. Soc., 1938, 60, 2142—2148; cf. A., 1934, 1349).—Formation of lactones from and hydrolysis to β -OH-acids is shown to proceed without Walden inversion by the use of cyclic diastereoisomeric acids, the configurations of which are rigidly proved. *cis-cycloHexane-1 : 2-dicarboxylic anhydride* (I), m.p. 31°, b.p. 161.7—161.9°, is prepared from $o\text{-C}_6\text{H}_4(\text{COMe})_2$ and H_2 -Raney Ni at 225°/133 atm., but is better obtained by condensing $(\text{CH}_2\cdot\text{CH})_2$ and $(\text{CH}\cdot\text{CO})_2\text{O}$ in C_6H_6 and hydrogenating (PtO_2) the product in AcOH ; when heated with HCl at 180° and then with AcCl it yields the *trans*-anhydride (II), m.p. 140—142°. With PhBr and AlCl_3 (I) gives *cis-2-p-bromobenzoylcyclohexane-1-carboxylic acid* (III) (83%), m.p. 169—171° (*Me ester*, m.p. 60—61°), which with $\text{Ac}_2\text{O}-\text{AcOH}$ and a drop of H_2SO_4 at 0—10° or $\text{AcOH}-\text{Ac}_2\text{O}$ at 60—65° gives α -acetoxy- α -p-bromophenyl-*cis-hexahydrophthalide* (IV), m.p. 149°, hydrolysed by hot, moist Et_2O or by aq. $\text{NaHCO}_3-\text{Et}_2\text{O}$ to (III). *trans-2-p-Bromobenzoylcyclohexane-1-carboxylic acid* (V) [similarly obtained from (II) in 60% yield], m.p. 164° (*Me ester*, m.p. 98—99°), gives the *trans-isomeride* (VI), m.p. 96—97°, of (IV) only by $\text{H}_2\text{SO}_4-\text{Ac}_2\text{O}$ and is formed from (III) by acids, or, since it can enolise, also by hot 5% aq. Na_2CO_3 . (VI) is more stable than (IV) and it is hydrolysed (dil. acids) to (V). With Ac_2O and a little H_2SO_4 (III) or (V) can also give the *lactone* (VII), $[\text{CH}_2]_4\langle\text{CH}\cdot\text{CO}\rangle_{\text{C}(\text{C}_6\text{H}_4\text{Br})}\text{O}$, m.p. 95°, hydrolysed by KOH to (V) [any (III) formed being isomerised]. In CCl_4 (VII) gives only the *trans-dibromide* (VIII), m.p. 119—122°, which is hydrolysed by moist air or, more rapidly, by dil. AcOH to 2-bromo-2-*trans-p-bromo-*

benzoylcyclohexane-1-carboxylic acid (IX), m.p. 147°, and by ROH to the *Me*, m.p. 93°, and *Et*, m.p. 115°, *ethers* of 2-bromo- α -hydroxy- α -p-bromophenylhexahydrophthalide. With Ac_2O (VIII) gives 2-bromo- α -acetoxy- α -p-bromophenyl-trans-hexahydrophthalide (X), m.p. 174—176° (decomp.), which is also obtained from (III) or (V) by $\text{Br}-\text{Ac}_2\text{O}$ and is hydrolysed, best by hot $\text{HCl}-\text{AcOH}$, to (IX). With $\text{Br}-\text{Ac}_2\text{O}-\text{AcOH}$ (III) gives slowly (X) and the *cis-isomeride* (XI), m.p. 149°, the latter product yielding by hydrolysis 2-bromo-*cis*-2-p-bromobenzoylcyclohexane-1-carboxylic acid (XII), m.p. 185—187° (decomp.) (*Me* ester, m.p. 106°). With Ac_2O or $\text{Ac}_2\text{O}-\text{AcOH}$ under various conditions (XII) readily gives (XI), but prep. of (X) from (IX) requires $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$; in Ac_2O at room temp. (XII) gives an *isomeride*, m.p. 78°, of (XI) (isomerism at C_α). When shaken in Et_2O with 1% aq. NaHCO_3 (IX) (in which Br and CO_2H are *cis*) gives the β -lactone (XIII), m.p. 83°, of (XIV) (below) stable to hot MeOH, converted by $\text{HBr}-\text{COMe}_2$ into (IX) and by 1% aq. KOH into 2-hydroxy-2-trans-p-bromobenzoylcyclohexane-1-carboxylic acid (XIV), m.p. 134°, stable to acid and alkali, the *Me* ester (prep. by CH_2N_2), m.p. 88°, of which with NaOMe or $\text{H}_2\text{SO}_4-\text{MeOH}$ gives an *ester*, m.p. 142°, also obtained from (XIII) by a trace of NaOMe in MeOH. With more NaOMe in MeOH (XIII) gives 2-hydroxy-2-*cis*-p-bromobenzoylcyclohexane-1-carboxylic acid (XV), m.p. 187° (*Me* ester, m.p. 54°, prepared by CH_2N_2 or $\text{MeOH}-\text{H}_2\text{SO}_4$). With Ac_2O at room temp. (XV) gives 77% of 2-hydroxy- α -acetoxy- α -p-bromophenyl-*cis*-hexahydrophthalide, m.p. 95° [with $\text{HCl}-\text{AcOH}$ regenerates (XV)], but (XIV) is unaffected. R. S. C.

Friedel-Crafts reactions on *m*-diphenylbenzene. H. G. GOODMAN, jun., and A. LOWY (J. Amer. Chem. Soc., 1938, 60, 2155—2157).— $\text{m}-\text{C}_6\text{H}_4\text{Ph}_2$, AcCl or Ac_2O , and AlCl_3 in PhNO_2 give *p'*-acetyl-*m*-diphenylbenzene, m.p. 104° [oxidised by CrO_3 to *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ (I) and by NaOCl to *m*-diphenylbenzene-*p*-carboxylic acid, m.p. 221°, which with AcCl and AlCl_3 in PhNO_2 gives *p'p''*-diacetyl-*m*-diphenylbenzene, m.p. 152° [oxidised to (I); not obtained directly from $\text{m}-\text{C}_6\text{H}_4\text{Ph}_2$]. BzCl in PhNO_2 gives similarly *p'*-benzoyl-*m*-diphenylbenzene, m.p. 117° (oxidised to *p*- $\text{C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$), $\text{CH}_2\text{Cl}\cdot\text{COCl}$ in CS_2 gives *p'p''*-di(chloroacetyl)-*m*-diphenylbenzene, m.p. 150° [oxidised to (I)], PhSO_2Cl (no solvent) gives *p'*-benzenesulphonyl-*m*-diphenylbenzene, m.p. 119° (oxidised to *p*- $\text{PhSO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$), and *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ gives *x-o*-carboxybenzoyl-*m*-diphenylbenzene [*"m*-diphenylbenzenephthaloylic acid"] (no identifiable oxidation products; ring-closure only effected by H_2SO_4 at 136° with sulphonation). R. S. C.

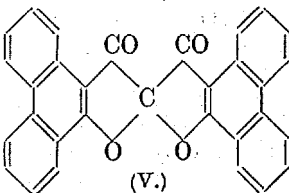
Action of magnesium methyl halides on 2:4:6-trisubstituted benzoyl chlorides. R. C. FUSON, J. H. VAN CAMPEN, and D. E. WOLF (J. Amer. Chem. Soc., 1938, 60, 2269—2272).—*o*-Halogen suppresses the formation of benzil derivatives from aryl halides and MgMeHal . 2:4:6- $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{COCl}$ and MgMeBr (2 mols.) give $\text{CH}_2(\text{CO}\cdot\text{C}_6\text{H}_2\text{Cl}_3)_2$ (*Br*-derivative, m.p. 163—164°), the structure of which is proved by regeneration from its *Br*-derivative by $\text{HCl}-\text{KI}-\text{COMe}_2$. 2:4:6- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{COCl}$ (I) and MgMeBr or MgMeI give *di*-2:4:6-tribromobenzoyl-

methane (II), m.p. 244—245° (decomp.) [*Br*-derivative, decomp. 282° (block), 274—276° (sinters at 266°; tube), prep. by $\text{Br}-\text{CHCl}_3$ or NaOBr , reduced to (II)], and a small amount of the probable intermediate 2:4:6- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{COMe}$ (III). When heated first with MgMeI and then with (I), (III) gives 54% of (II). 4:2:6- $\text{C}_6\text{H}_2\text{MeBr}_2\cdot\text{COCl}$ and MgMeI give 3:5-dibromo-4-acetotoluene, m.p. 53—54° (*CHPh*: derivative, m.p. 96—97°). R. S. C.

Coupling action of the Grignard reagent. VI. Synthesis of hexa-alkylbenzils. R. C. FUSON and J. CORSE (J. Amer. Chem. Soc., 1938, 60, 2063—2066).—The alkylation of RCOCl by MgMeI (to give COMeR) is diminished and the coupling [to give $(\text{COR})_2$ and C_2H_6] is increased if R is a sterically hindered aryl and if MgMeI is added to RCOCl in much Et_2O . Only alkylation occurs if RCOCl is added to MgMeI . Thus, 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{COCl}$ gives 39% of $(\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO})_2$ and 35% of $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{COMe}$, and 2:4:6-triethylbenzoyl chloride, b.p. 112—113°/4—5 mm., gives 32.5% of 2:4:6:2':4':6'-hexaethylbenzil, m.p. 75—75.5°, and 38.4% of 2:4:6-triethylacetophenone, b.p. 115—118°/5 mm. [3:5- $(\text{NO}_2)_2$, m.p. 112—113°, and ω -*CHPh*: derivative, m.p. 66°] (obtained also from *s*- $\text{C}_6\text{H}_3\text{Et}_3$, Ac_2O , and AlCl_3 in hot CS_2). *s*- $\text{C}_6\text{H}_3\text{Et}_3$, Br, and Fe in CCl_4 give 2-bromo-1:3:5-triethylbenzene, b.p. 96—99°/2—3 mm. [4:6- $(\text{NO}_2)_2$ -derivative, m.p. 78.5—79°], converted (Grignard- CO_2) into 2:4:6-triethylbenzoic acid, m.p. 113—113.5°. R. S. C.

Polymerisation processes caused by pyridine.

II. Formation of a blue 1:2:3-triketone from phenanthraquinone. O. DIELS and R. KASSEBART (Annalen, 1938, 536, 78—88; cf. A., 1938, II, 353).—The main product of the action of Ac_2O and NaOAc on phenanthraquinone (I) (Scharwin, A., 1905, i, 448) is $\text{C}_{32}\text{H}_{18}\text{O}_7$ (not $\text{C}_{33}\text{H}_{22}\text{O}_7$ or 20O_7). It is 9:9'-diphenanthryl ether-10:10'-di(glyoxylic acid) (II) since it passes when heated with alkali into the orange lactone (Meyer and Spengler, A., 1905, i, 219, 362) readily prepared from (I) and $\text{KOH}-\text{EtOH}$. (II) loses H_2O and CO at $\sim 280^\circ$ in N_2 to give the blue 9:9'-oxido-10:10'-diphenanthryl triketone (III), decomp. $\sim 340^\circ$, obtained in small amount from (I), Ac_2O , and NaOAc (Scharwin *loc. cit.*), but as main product when (I) is heated with Ac_2O and $\text{C}_5\text{H}_5\text{N}$ in the dark. The constitution of (III) is supported by the ready loss of CO under the influence of light with production of 9:9'-oxido-10:10'-diphenanthryl diketone (IV), m.p. $>360^\circ$. Further (III) with NH_2Ph gives the additive product, $\text{C}_{37}\text{H}_{23}\text{O}_4\text{N}$, m.p. $>360^\circ$ [*Ac* derivative (+ AcOH), gradual decomp. $>300^\circ$ after much softening at about 192—195°], and with NHPhMe yields the substance, $\text{C}_{38}\text{H}_{25}\text{O}_4\text{N}$; in boiling PhNO_2 these pass into (IV). With Ac_2O and $\text{C}_5\text{H}_5\text{N}$ at 160° (sealed tube) (I) yields the spiran (V), m.p. $\sim 400^\circ$ (decomp.) after softening, which gives a red colour in conc. H_2SO_4 . (III) and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ give the quinoxaline derivative, $\text{C}_{37}\text{H}_{20}\text{O}_2\text{N}_2$, m.p. $>360^\circ$.



Warm KOH transforms (III) into a red substance

(VI), m.p. 252—254° (decomp.) [which readily re-forms (HI) and yields (Ac₂O with a little H₂SO₄) a diacetate, m.p. 298—300° (decomp.)], and a yellow compound (VII) (+1AcOH), which has no tendency to revert to (III) and is transformed by boiling Ac₂O into (V). (VI) and (VII) are formulated as 9 : 9'-*dihydroxy*-10 : 10'-*diphenanthryl triketone* α - and β -hydrate, respectively.

H. W.

Estrone *n*-octoate, m.p. 70—71°, and laurate, m.p. 69.5—70°.—See A., 1938, IH, 908.

Ergostatrienone, m.p. 131—132.5°.—See B., 1938, 1230.

Unsaturated keto-alcohols of the androstane and pregnane series, $\beta\gamma$ -unsaturated ketones of the cyclopentanopolyhydrophenanthrene series, and pregnenediones.—See B., 1938, 1230.

Astaxanthin and ovoverdin. R. KUHN and N. A. SÖRENSEN (Ber., 1938, 71, [B], 1879—1888).—Partly a more detailed account of work previously reviewed (A., 1938, II, 328). The following appears new. The 2 OH groups in astaxanthin (I) are readily demonstrated by prep. of the diacetate (II), m.p. 203—205° (vac.), didecoate, m.p. (indef.) 121—124 (vac.), and dipalmitate, m.p. 71.5—72.5°. A tetra-ester could not be obtained. In harmony (I) gives 2 mols. of CH₄ with MgMeI whereas (II) yields none. The two active H atoms of astacin (III) result from the repeated arrangement $\cdot\text{CH}_2\cdot\text{CO}\cdot$; with (I) only the two alcoholic OH are active in the Zerevitinov determination and in ester formation. The hypothesis that the two CO of (I) are not vicinal to CH₂ explains immediately why its distribution between light petroleum and aq. MeOH, in contrast with that of (III), is unaffected by NaOH. It is therefore very possible that the two CO are in $(\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}\langle\text{CMe}_2\cdot\text{CH}_2\rangle\text{CH}\cdot\text{OH})_2$ (A),

conjugation to the polyene chain thus leading to the structure (A) for (I). The dark blue alkali salts of (I) (*loc. cit.*) appear to be the result of double enolisation. When decomposed by dil. H₂SO₄ in a high vac. they reform (I) exclusively. Reasons for the non-autoxidation of ovoverdin, *M* ~ 144,000 (determined chemically), are discussed. The epiphagic pigment of the lobster hypodermis is an ester of (I), not (III) as supposed (A., 1933, 509). Further the chromoproteins of the shell give (I) when decomposed by heat or by dil. acid. The pigment of the boiled lobster is therefore (I), not (III). This is probably the case with all crustaceæ unless putrefaction or other influences induce alkaline reaction which renders possible the autoxidation to tetraketone, i.e., (III), in boiling solution. H. W.

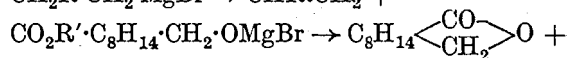
Keto-phenols, new class of compounds in Australian essential oils. F. REUTER (J. Proc. Austral. Chem. Inst., 1938, 5, 289—290).—*Macro-pone*, a liquid keto-phenol, C₁₀H₁₂O₂ (semicarbazone, m.p. 216°; 2 : 4-dinitrophenylhydrazone, m.p. 243°; phenylhydrazone, m.p. 85°; *Me ether semicarbazone*, m.p. 216°; *benzoate semicarbazone*, m.p. 173°), from *Eucalyptus cneorifolia* oil, gives a red colour with FeCl₃, a dye with PhN₂Cl, absorbs Br only very slowly, and gives no CHI₃ with NaOI. Another ketone (semicarbazone, m.p. ~188°; 2 : 4-dinitrophenylhydrazone, m.p. ~208°) from this oil gives a blue-green

FeCl₃ reaction. *E. polybracteæ* oil also contains keto-phenols. A. LI.

Action of oxalic acid on α -pinene in presence of boracetic anhydride. M. IMOTO (J. Soc. Chem. Ind. Japan, 1938, 41, 251—252B).— α -Pinene with H₂C₂O₄ and B(OAc)₃ yields borneol, terpene alcohols, and polymerised substances. The reaction requires careful control and cooling or explosion results. J. D. R.

Synthesis and study of monosubstituted β -campholides and their derivatives. J. VÈNE (Ann. Chim., 1938, [xi], 10, 194—279).—Modified directions are given for the conversion of camphor through oximinocamphor and camphorquinone into camphoraldehydic acid (I), C₈H₁₄(CHO)·CO₂H (cf. Bredt, A., 1917, i, 560; Salmon-Legagneur, A., 1932, 1037). It is converted by successive treatment with SOCl₂ and the requisite alcohol into the corresponding Me (II), b.p. 137—139°/16 mm., Et (III), b.p. 135—136°/10 mm., and CH₂Ph (IV), b.p. 206—208°/12 mm., esters. (II) is transformed by a large excess of MgMeI in Et₂O into β -methyl- β -campholide (V), C₈H₁₄ $\langle\text{CO}\rangle\text{CHMe}$, m.p. 178° (crystallographical data),

and non-cryst. products which probably contain OH·CHMe·C₈H₁₄·CMe·CH₂ but from which a homogeneous material could not be isolated. With MgEtI (II) affords mainly β -ethyl- β -campholide (VI), m.p. 78° (crystallographical data), with small amounts of β -campholide (VII), neutral substances, (?) OH·CHET·C₈H₁₄·CET·CHMe and OH·CHET·C₈H₁₄·CET₂·OH, and an acid, m.p. 121—122°, probably CO₂H·C₈H₁₄·CET₂·OH or CO₂H·C₈H₁₄·CHET·OH. From (I) and MgEtBr only (VI) could be obtained; this is also derived from (III) or (IV). From MgPr^aBr and (II) the main product is (VII) accompanied by β -propyl- β -campholide, m.p. 41°, [α]_D²⁵ —65.9° in abs. EtOH, and an acid, probably CO₂H·C₈H₁₄·CPr^a·OH, m.p. about 115°. The reducing action is probably CO₂R'·C₈H₁₄·CHO + CH₂R'·CH₂·MgBr → CHR'·CH₂ +



OR'·MgBr. MgPr^bBr and (H) yield (VII) and, apparently, β -isopropyl- β -campholide, b.p. 163—164°/14 mm., [α]_D²⁵ —40.7° in EtOH. Much reduction occurs with (II) and MgBu^bBr but β -butyl- β -campholide, b.p. 178—180°/16 mm., [α]_D²⁵ —52.6° in EtOH, can be isolated. MgPhBr (2 mols.) and (II) afford β -phenyl- β -campholide, m.p. 212° (block), [α]_D²⁵ —31.7° in CHCl₃. CH₂Ph·MgCl and (II) yield mainly β -benzyl- β -campholide, m.p. 102°, [α]_D²⁵ —146° in EtOH, and a liquid from which a homogeneous material could not be isolated. The campholides are generally stable to heat. With cold, conc. H₂SO₄ (V) and (VI) give non-cryst. products identical in composition with the initial materials but with much lower [α]_D. (VI) like (VII) is very resistant to HBr·AcOH but gives a small proportion of an acid, (?) CO₂H·C₈H₁₄·CHETBr, m.p. about 110° (decomp.), readily converted by aq. Na₂CO₃ into (VI). Analogously (V) gives a very unstable *Br-acid*, m.p. about 170° (decomp.). Na in boiling EtOH reduces (V) to the glycol, OH·CH₂·C₈H₁₄·CHMe·OH, m.p. 108°; the corresponding glycol from (VI) could not be obtained pure. Treatment of the requisite cam-

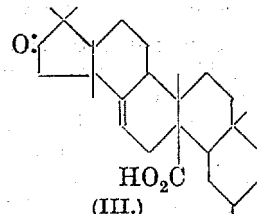
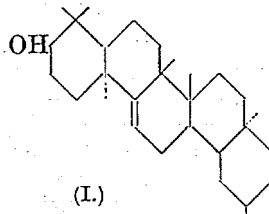
pholide in EtOH-H₂O with NaOH, removal of EtOH, and addition of HCl to the residual solution until it is just acid to Congo-red gives the following acids: β -hydroxy- β -methyl-[2 : 2 : 3-trimethyl-3- α -hydroxyethylcyclopentane-1-carboxylic], m.p. 135°, $[\alpha]_D^{25} +61.2^\circ$ in EtOH, β -ethyl-, three forms, m.p. 73°, 87° and 105° respectively (interconversions described), β -propyl-, m.p. 112°, $[\alpha]_D^{25} +20.4^\circ$ in EtOH, β -phenyl-, m.p. 166°, $[\alpha]_D^{25} +32.9^\circ$ in EtOH, and β -benzyl-campholic acid, m.p. 154—155°, $[\alpha]_D^{25} +2.7^\circ$ in EtOH. The acids are stable under ordinary conditions and do not pass spontaneously into the corresponding substituted β -campholide; the change occurs readily when they are heated somewhat above their m.p., or when treated with Ac₂O or SOCl₂. The rates of opening of the lactone ring of (V) and (VI) by aq. NaOH at 48° are very similar and \ll that of (VII), which in turn is \ll that of α -campholide. In EtOH-H₂O at 60° this difference is less marked. The rate of opening of the ring of substituted campholides depends considerably on the nature of the substituting radical. In EtOH-H₂O at room temp. or at 35° the ring of (V) is opened appreciably less slowly than that of (VI). The rate of lactonisation of β -substituted β -hydroxy-campholic acids is \ll that of the parent acid. Lactonisation in H₂O at about 100° takes place only in the presence of mineral acids as catalysts and is then a change of the first order. (II) and saturated aq. NaHSO₃ give the somewhat unstable cryst. *H* sulphite compound, transformed by KCN into *Me* 2 : 2 : 3-trimethyl-3-cyanohydroxymethylcyclopentane-1-carboxylate (VIII), m.p. 127°, $[\alpha]_D^{25} +46.8^\circ$ in EtOH. The NaHSO₃ compound from (III) could not be caused to crystallise but its aq. solution gives the nitrile-ester (IX), CO₂Et·C₈H₁₄·CH(OH)·CN, m.p. 97°, $[\alpha]_D^{25} +36.8^\circ$ in EtOH. The compounds CO₂CH₂Ph·C₈H₁₄·CH(OH)·CN and CO₂H·C₈H₁₄·CH(OH)·CN could not be obtained. 92% H₂SO₄ at about 100° converts (VIII) into β -carboxylamido- β -campholide (X), m.p. 262° (block), $[\alpha]_D^{25} -73.5^\circ$ in AcOH (yield 85%), also obtained from (IX), whereas 80% H₂SO₄ at about 100° gives β -cyano- β -campholide (XI), m.p. 228° (block), $[\alpha]_D^{25} -56.5^\circ$ in EtOH (crystallographic data). A large excess of boiling conc. KOH converts (VIII) into 2 : 2 : 3-trimethyl-2-hydroxycarboxylamidomethylcyclopentane-1-carboxylic acid (XII), m.p. 143°, $[\alpha]_D^{25} +22.8^\circ$ in AcOH, whereas more drastic treatment appears to give β -carboxy- β -campholide (XIII), m.p. 213° (block), $[\alpha]_D^{25} -77.8^\circ$ in EtOH. (XII) is converted into (XI) by Ac₂O at about 120° or by SOCl₂; the reverse transformation is easily effected by dil. NaOH. (X) is transformed by boiling 20% H₂SO₄ into the corresponding acid amide. Gradual addition of NaNO₂ to (X) in well-cooled 92% H₂SO₄ which is subsequently heated at 70—80° leads to (XIII). This is converted by boiling NaOH-H₂O-EtOH and subsequent exact acidification into 2 : 2 : 3-trimethyl-1-carboxycyclopentane-3-glycollic acid, m.p. 198°, $[\alpha]_D^{25} +10.8^\circ$ in EtOH. H. W.

Synthesis of ethylisocamphylamine. P. LIPP and H. BRÄUCKER (Ber., 1938, 71, [B], 1808—1809). —*iso*Camphylamine hydrochloride is transformed by EtBr and KOH in boiling EtOH into *ethylisocamphyl-*

amine (I), b.p. 96—97°/9 mm. [*NO*-derivative, b.p. 122—124°/0.6 mm.; hydrochloride, and phenylcarbamide, m.p. 120.5—121°, identical with the products of Lipp *et al.* (A., 1936, 1384); *platinichloride*]. H. W.

Betulenols. III. Methyl-oxidation of caryophyllene to caryophyllenol. W. TREIRS (Ber., 1938, 71, [B], 1794—1797; cf. A., 1938, II, 195).—Caryophyllene (I), $\alpha_D -9^\circ$, from carnation stalk oil, reacts very slowly with SeO₂ when suspended in boiling Ac₂O, giving *caryophyllenyl acetate* (II), b.p. 170—180°/20 mm., and leaving much hydrocarbon, $\alpha_D -18^\circ$, which is not oxidised by SeO₂ and is decomposed when heated. Hydrolysis of (II) affords *caryophyllenol* (III), b.p. 157—159°/20 mm., $[\alpha]_D^{25} -14.5^\circ$ (non-cryst. *phenylcarbamate* and *benzoate*), purified through the non-cryst. *H* phthalate. The behaviour of (III) towards oxidising agents resembles that of the betulenols (IV), conversion into the corresponding aldehyde and monocarboxylic acid by CrO₃ appearing impossible since immediate action occurs at the double linking. A large excess of KMnO₄ transforms (III) into products sol. in alkali hydroxide and converted by the protracted action of hot, dil. HNO₃ into CO₂H·CMe₂·CH₂·CO₂H and homocaryophyllenic acid identical with that derived from (IV) (*loc. cit.*). (III) and the ketocarboxylic acid of Ruzicka and Wind (A., 1931, 734) and Ramage and Simonsen (A., 1936, 994) appear to be derived from the same component of (I). H. W.

Triterpenes. XXXIX. Fission of ring A of oleanolic acid. L. RUZICKA and F. C. VAN DER SLUYS-VEER (Helv. Chim. Acta, 1938, 21, 1371—1383; cf. A., 1938, II, 150).—Revision of the work of Kitasato (A., 1937, II, 462) strengthens the author's formula (I) for oleanolic acid (I). The bromolactone of (I) is converted by CrO₃ (=2 O) in AcOH at room temp. into oleanonic acid bromolactone, m.p. 246—247° (*oxime*, m.p. 251—252°), further oxidised (CrO₃-H₂SO₄-AcOH) to the bromolactone of oleanoltricarboxylic acid, m.p. 267—268°, which, contrary to



Kitasato (*loc. cit.*), appears to be the sole product of the change. It is converted by CH₂N₂ in Et₂O into *Me*₂ *H* oleanoltricarboxylate bromolactone, m.p. 187—188°, debrominated (Zn dust in boiling AcOH) to *Me*₂ *H* oleanoltricarboxylate, m.p. 216—217°, $[\alpha]_D +60^\circ$ in CHCl₃, whence successively *Me*₃ oleanoltricarboxylate (II), m.p. 170—171°, $[\alpha]_D +56^\circ$ in CHCl₃, and oleanoltricarboxylic acid, m.p. 290—291°. This loses CO₂ at 310° and gives the *keto-acid* (III), m.p. 318—319° [*Me* ester (IV), m.p. 185—186°, unusually re-

sistant towards alkaline hydrolysis, and its *oxime*, m.p. 204—206°, converted by Br in MeOH-CCl₄ into the *bromolactone*, C₂₅H₄₃O₃Br, m.p. 236—237°. The conversion of (II) into (IV) and thence into (III) is described.

H. W.

Triterpenes. XL. Acidic product of the oxidation of esters of lupeol. L. RUZICKA, H. SCHELENBERG, and G. ROSENKRANZ (Helv. Chim. Acta, 1938, 21, 1391—1394; cf. A., 1938, II, 23).—Oxidation of lupeol acetate under conditions differing somewhat from those adopted by Heilbron *et al.* (A., 1938, II, 195) gives a non-homogeneous neutral product containing the keto-acetate described by these authors, and an acetylated acid (I), m.p. 302—303° (vac.) [*Me* ester (II), m.p. 262—264° (vac.), and *Ac*-free acid (III), m.p. 291—292° (vac.)]. Lupeol benzoate is similarly oxidised to an acid, m.p. 328—329° (vac.) (*Me* ester, m.p. 273°). Analyses of (III) indicate the formula C₃₀H₄₈ or C₃₀H₅₀O₃. (I) and (II) do not give a colour with C(NO₂)₄, but this does not exclude with certainty the presence of an αβ-unsaturated acid. The absorption spectrum definitely excludes such a grouping, which also appears excluded by the impossibility of hydrogenating (PtO₂ in AcOH-EtOAc) the acid or ester. The latter substance is stable to o-CO₂H·C₆H₄·CO₂H. It is most probable that (I) is C₃₀H₅₀O₃ or C₂₉H₄₈O₃ if a C has been lost. All m.p. are corr.

H. W.

Triterpene group. II. Carbon skeleton of the triterpenes. J. C. E. SIMPSON (J.C.S., 1938, 1313—1317).—The compound C₃₀H₄₄OS (I) obtained by mild dehydrogenation of β-amyrin with S (cf. Jacobs *et al.*, A., 1930, 1292) gives an *acetate*, m.p. 197.5—198.5° and 201—202°, [α]_D²⁵ +111° in CHCl₃, which yields results on quant. saponification indicating that the whole of the original C skeleton is present in (I). This observation is irreconcilable with any skeleton formula hitherto advanced for the oleanolic acid group of triterpenes. Oxidation (KMnO₄) of the acetate gives the ketone, C₃₀H₄₄O₃, m.p. 282—283° (lit. C₃₀H₄₆O₃, m.p. 274—275°), the acetate of which on oxidation affords a lactone-acetate, C₃₂H₄₄O₅, reduced (Na-C₅H₁₁·OH) to an acid, C₃₀H₅₀O₄, m.p. 252—254° (*Me* ester diacetate, m.p. 217—219°). The relationship between these compounds is elucidated.

F. R. S.

Structure of the triterpenes. J. H. BENYON, I. M. HEILBRON, and F. S. SPRING (Nature, 1938, 142, 434—435).—Dehydrogenation (Se) of basseol (I) gives chiefly a phenanthrene *homologue*, C₁₇H₁₆, m.p. 125°, probably a trimethylphenanthrene (different from ones known) (picrate, m.p. 165°), apparently the hydrocarbon "C₁₈H₁₈" obtained by Ruzicka *et al.* (A., 1934, 530) from hederagenin. Two partial structures for (I) are given. The structure suggested by Ruzicka *et al.* (A., 1938, II, 23) is incorrect.

L. S. T.

Crystallographic investigations in the terpene group.—See A., 1938, I, 440.

Constitution of resin phenols and their biogenetic relationships. VII. Unsymmetrical substitution products of eudesmin and pinoresinol dimethyl ether. H. ERDTMAN (Svensk

Kem. Tidskr., 1938, 50, 161—167).—*d*-Sesamin with alkali followed by Me₂SO₄ yields pinoresinol Me₂ ether (I) and an isomeride, m.p. 132—134°. Pinoresinol with EtOH-HCl followed by Me₂SO₄ gives (I) and an isomeride, m.p. 131—133°, [α]_D²⁵ +140° in CHCl₃ [(NO₂)₂-derivative, dimorphous, m.p. 160—163° and 180—182°]. Eudesmin and (I) with HNO₃-AcOH-Ac₂O yield NO₂-derivatives, m.p. 169.5—171.5°, [α]_D²⁵ +147° and —145° respectively in CHCl₃, the mixture, m.p. 158—160°, being inactive. These with HBr give *bromonitro*-derivatives, m.p. 180—181°, [α]_D²⁵ +182° and —180° respectively in CHCl₃, which when crystallised together give a racemate, m.p. 200—201°.

A. LI.

Composition and biogenesis of original resin acids. W. SANDERMANN (Ber., 1938, 71, [B], 2005—2014).—The balsam of coniferae contains essentially *d*- (I) and *l*- (II) -pimaric acid, proabietic acid, and possibly a small amount of abietic (sylvic) (III) acid. Except (I) all of these are isomerised by mineral acid to (III). The content of (I) can therefore be determined by observation of [α]_D after isomerisation. (II) can be determined by the diene synthesis with maleic anhydride (IV) or *p*-benzoquinone (V) at room temp. followed by acidimetric or iodometric determination of the residual reagent or by optical measurement. The acids are present in about the same proportion in the cryst. mixture as in the balsam. Strictly, (I) and (II) are the only original resin acids; of these (II) becomes more or less isomerised under the influence of the acidity of the plant and of warmth. There is no evidence that the acids are formed from an aldehyde, C₁₀H₁₆O. Fresh balsam does not give aldehydic reactions. (IV) and (V) give the adducts of (II) and acid val. and content of (II) are the same in liquid and cryst. balsams. There is therefore no doubt that the resin acids are preformed in the effluent balsam. Surface forces have an outstanding influence on the crystallisation of the balsams, which can remain almost transparent and liquid for weeks in vessels coated with agar, starch, collodion, gelatin, or gum arabic whereas crystallisation begins in 1—8 hr. in glass tubes. Biogenesis of the resin acids appears to depend on "methyl oxidation," the sequence of hydration and dehydration, and finally in the vinylcarbinol isomerism.

H. W.

Saponins and sapogenins. VIII. Surface films of echinocystic acid and [its] derivatives. C. R. NOLLER (J. Amer. Chem. Soc., 1938, 60, 1938—1939; cf. A., 1938, II, 372).—Echinocystic acid, its *Me* ester and diacetate give incompressible films of 58, 56, and 54 sq. A., respectively, contracting at low pressures. Echinocystadienol gives a film of 45 sq. A. A close relationship to hederagenin (I) is indicated. These film areas support Kitasato's formula for (I) (A., 1937, II, 462).

R. S. C.

Echinochrome and spinochrome. E. LEDERER and (MLLE.) R. GLASER (Compt. rend., 1938, 207, 454—456).—Aq. COMe₂ containing 1% of AcOH extracts *echinochrome*, C₁₂H₁₀O₇ (I), m.p. 220°, from the ovaries of *Arbacia aequituberculata*, Bl. 1—1.5 mg. of cryst. pigment (isolation described) is obtained from each animal. The mol. contains 4

reactive H (Grignard reagent), two of which are probably phenolic. There are 2 aromatic Me. The violet pigment of *Strongylocentrotus lividus* is separated by adsorption on CaCO_3 into (I) and *spinochrome*, $\text{C}_{12}\text{H}_{10}\text{O}_8$, m.p. about 185° , which contains 5 reactive H and 4 aromatic Me. It is decolorised by $\text{Na}_2\text{S}_2\text{O}_4$ and reoxidised in air. J. L. D.

Biochemistry of the lower fungi. II. Constitution and syntheses of phoenicin and new derivatives of 4:4'-ditoluquinone. T. POSTERNAK (Helv. Chim. Acta, 1938, 21, 1326—1337).—Phoenicin (I), m.p. $230\text{--}231^\circ$ when heated rapidly, obtained by extraction of *Penicillium phoeniceum* with CHCl_3 , is $\text{C}_{14}\text{H}_{10}\text{O}_6$. It is strongly acidic (K_1 and NH_4 salts) owing to the presence of 2 phenolic or enolic OH and gives a neutral diacetate, m.p. $117\text{--}118^\circ$. With quinol it gives an additive compound, $\text{C}_{14}\text{H}_{10}\text{O}_6 \cdot 2\text{C}_6\text{H}_6\text{O}_2$, m.p. $198\text{--}200^\circ$ (in sealed capillary containing rarefied CO_2), and with toluquinol a substance, m.p. 160° . It is largely destroyed by oxidising agents but the isolation of 2 mols. of AcOH establishes the presence of two $\cdot\text{CMe}\cdot\text{C}<$ groups. (I) suspended in H_2O is readily hydrogenated (Pd-black) to leucophoenicin (II), $\text{C}_{14}\text{H}_{14}\text{O}_6$, m.p. 247° (decomp.) [hexa-acetate (III), m.p. $202\text{--}203^\circ$; tetrabenzoate, m.p. $212\text{--}214^\circ$], re-oxidised to (I) by FeCl_3 , *p*-benzoquinone, or air. With cyclopentadiene in boiling EtOH (I) readily yields dicyclopentadienephoenicin, m.p. 181° (decomp.) after becoming intensely yellow at about 165° . 4:4'-Ditoluquinone is transformed by Ac_2O containing conc. H_2SO_4 at room temp. into (III) and leucoisophoenicin hexa-acetate, m.p. 182° . Hydrolysis ($\text{HCl}\text{--}\text{MeOH}$) of (III) gives (II), readily oxidised to (I), which is therefore 4:4'-dimethyl-2:2'-dihydroxydiquinone. It is converted by cold $\text{Ac}_2\text{O}\text{--}\text{H}_2\text{SO}_4$ into anhydrodihydroxy-leucophoenicin hexa-acetate, m.p. about 256° , hydrolysed to anhydrodihydroxy-leucophoenicin, m.p. $343\text{--}348^\circ$ (block), whence anhydrodihydroxyphoenicin, decomp. about 300° (block). Leucoisophoenicin, m.p. $255\text{--}258^\circ$, and isophoenicin, m.p. $213\text{--}215^\circ$ (decomp.) (diacetate, m.p. $204\text{--}205^\circ$), are described. H. W.

Crotoxin from rattlesnake venom.—See A., 1938, III, 815.

Coffee. III. Isolation of cafesterol and other compounds from the unsaponifiable matter from coffee oil. K. H. SLOTTA and K. NEISSER (Ber., 1938, 71, [B], 1991—1994).—Raw coffee is extracted with Et_2O , the extract is evaporated and the solution of the residue in light petroleum is kept at 0° , whereby caffeine separates. The solution is evaporated and the residue is hydrolysed with 10% aq. NaOH. The unsaponifiable matter is removed by Et_2O and the cryst. residue is separated by light petroleum into a sol. and an insol. fraction. The latter contains cafesterol, $\text{C}_{20}\text{H}_{28}\text{O}_3$, m.p. $155\text{--}157^\circ$, $[\alpha]_D^{20} -137.9^\circ$ in CHCl_3 , which slowly becomes discoloured when kept, more rapidly in the light than in the dark, when O_2 has no influence. It is stable towards conc. alkali at 120° , but very sensitive towards acids. It gives an acetate. The presence of γ -sitosterol and of substances A, $\text{C}_{22}\text{H}_{34}\text{O}_2$, m.p.

$114\text{--}116^\circ$, C, m.p. $128\text{--}129^\circ$, I, m.p. $88\text{--}89^\circ$ and S, m.p. $62\text{--}64^\circ$, is also established. H. W.

Lignin. XI. Lignin from wheat straw. M. PHILLIPS and M. J. GOSS (J. Biol. Chem., 1938, 125, 241—246; cf. A., 1936, 994).—NaOH—EtOH removes from wheat straw, previously extracted with 1:2-EtOH— C_6H_6 , a lignin, $\text{C}_{38}\text{H}_{36}\text{O}_{12}(\text{OMe})_4$ (Ac₅ derivative), converted by 12% HCl into CH_2O and a product, which with CH_2N_2 yields an ether, $\text{C}_{38}\text{H}_{31}\text{O}_7(\text{OH})_2(\text{OMe})_7$, with $\text{Me}_2\text{SO}_4\text{--aq. NaOH}$ yields an ether, $\text{C}_{38}\text{H}_{31}\text{O}_7(\text{OH})(\text{OMe})_8$, with KOH— H_2O —Zn dust gives protocatechuic acid, and with Cl_2 in CCl_4 gives a product, $\text{C}_{42}\text{H}_{32}\text{O}_{16}\text{Cl}_{16}$. Subsequent extraction of the straw with 4% aq. NaOH gives a lignin, $\text{C}_{40}\text{H}_{42}\text{O}_{16}$ (Ac₄ derivative), and finally treating with hot 1% and then fuming HCl gives a product of higher (63.9%) C content. R. S. C.

Structure of lignin. A. B. CRAMER, M. J. HUNTER, and H. HIBBERT (J. Amer. Chem. Soc., 1938, 60, 2274).—Extraction of spruce wood by org. solvents yields a ketone, b.p. $140\text{--}150^\circ/0.004$ mm. (Me derivative, $\text{C}_{13}\text{H}_{18}\text{O}_4$, m.p. $81\text{--}82^\circ$; hydrazone), a polymeride, aldehyde, acid, neutral substance, and carbohydrate. The ketone yields veratric acid when oxidised and consists of a guaiacyl group and a C_3 side-chain containing a CO and OH. Hard woods give also syringyl derivatives. R. S. C.

Lignin. XVII. Degradation of pine lignin to phenolcarboxylic acids. K. FREUDENBERG, K. ENGLER, E. FLICKINGER, A. SOBER, and F. KLINK (Ber., 1938, 71, [B], 1810—1820; cf. A., 1937, II, 204).—Treatment of pine lignin (I) with alkali and subsequently with Me_2SO_4 in complete absence of O_2 does not lead to dehydrodiveratric acid (II), which arises from an unimportant but very sensitive component of (I). (II) may be reckoned as veratric acid (III). If methylated pine wood is used, 20% of (III), 4% of (II), and 6% (occasionally 12%) of isohemipinic acid (IV) are produced; 2:3:4-(OMe)₃C₆H₂·CO₂H is also formed in very small amount. Treatment of ethylated wood with KOH followed by ethylation and oxidation gives vanillic acid Et ether in up to 12% (of the lignin); the acid is more sensitive than (III) to oxidation. The estimated yields 34% of (II) + (III) and 80% of (IV) agree well with those calc. on the assumption that of every three units of (I) of "mol. wt." 178 one gives rise to (III) and the other two yield (IV). The amounts of isolated acids are thus in harmony with the hypothesis that (I) is derived from PhPr. The high *n* and the elementary composition also indicate the aromatic character. Cuproxam lignin (V) can be dissolved by repeated boiling with sulphite. Comparison of the yields of (III) and (IV) obtained therefrom by methylation and oxidation with those obtained similarly from (I) shows that the entrance of SO_3H so alters about one third of the components that the acids can be formed. The S content of the ligninsulphonic acid (VI) suggests that every third unit receives SO_3H in such a manner that the main product can yield (IV). Support is thus given to previous views (*loc. cit.*) on the constitution of (VI) and proof is afforded that SO_3H does not enter the C_6H_6 nucleus. Repeated treatment of (V) with 2%

HCl-MeOH at 100° causes dissolution of about half; the sol. portion gives 1.8% of CH₂O and has 20% OMe, increased to 33% OMe by use of CH₂N₂. Oxidation with KMnO₄ gives 2.5% of (III) and 1.7% of (IV). CH₂N₂ followed by Me₂SO₄ transforms wood into a product dissolved (except about 10%) by HCl-MeOH. The sol. portion is essentially the lignin component and when methylated and oxidised gives 3.5% of (III) and 2.5% of (IV). (I) is considerably demethylated by KNH₂ or K in liquid NH₃ to a phenolic product; this is not the sole reaction. N₂H₄ and (V) at 140° give a mobile, brown liquid; methylation and oxidation of the residue from this affords 6.5% of (IV) and 2.5% of (V). Under similar conditions pine wood gives a viscous, pale brown liquid which becomes a gel when cooled. (I) prepared by HCl-H₃PO₄ gives 2.5% of CH₂O when distilled with 28% H₂SO₄ whereas (V) and pine wood yield 3.8% and about 1% respectively. CH₂O therefore arises from the lignin component of wood and its origin from sugars or their decomp. products is impossible. It is produced either from aromatic CH₂O₂ groups or from side-chains. CHPh·CH·CH₂·OH gives under these conditions 2% of CH₂O whereas only traces are obtained from coniferin. H. W.

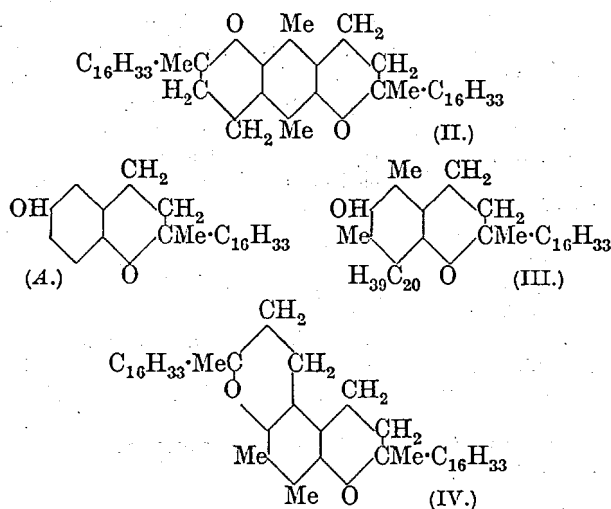
Lignin. XVIII. Beech lignin. K. FREUDENBERG and H. F. MÜLLER (Ber., 1938, 71, [B], 1821—1825).—Prolonged extraction of resin-free beech powder with cold 5% NaOH removes about 25% of polysaccharide material with low OMe content. Cold HCO₂H removes from the residue a small amount of material which according to solubility and OMe content resembles lignin closely. The residue affords a cuproxam lignin (I) with OMe 21.5%, C-Me 7.0% and CH₂O 1.4%. Treatment of beech wood with HCl-H₃PO₄ gives a HCl-lignin (II) very closely resembling (I) except for somewhat lower OMe content. Treatment of (II) with KOH-H₂O under N₂ at 210—215° and of the product with CH₂N₂ leads to methylated phenolic acids among which 2:3:4-(OMe)₂C₆H₂·CO₂H (III) predominates if the temp. has not exceeded 230°, whereas veratric acid (IV) appears in considerable amount if 270° is reached. Ethylation experiments show that the components of pyrocatechol appear in the vanillic acid skeleton, those of pyrogallol in the form of the syringic acid skeleton. Treatment of (II) with KOH-H₂O at 170°, methylation, and subsequent oxidation of the product yields isohemipinic acid (V) (III) and (IV). Methylated beech wood is transformed by KOH-H₂O, best at 190°, into (III), (IV), and (V). Similar treatment of ethylated beechwood affords the Et ethers of vanillic and syringic acid. H. W.

2-Carboxyfuryl-5-glycollic acid. E. VOTOČEK and A. KROŠLÁK (Coll. Czech. Chem. Comm., 1938, 259—263).—Ca δ-ketogluconate with MeOH-HCl yields the Me ester of aldehydopyromucic acid (A., 1934, 1008), which with NH₃ and HCN gives the *cyanohydrin*, m.p. 91.5°, hydrolysed [Ba(OH)₂] to 2-carboxyfuryl-5-glycollic acid (obtained from the Ba salt by conversion into the Pb salt and treatment with H₂S). A. LI.

Substituted methylchromones. H. A. OFFE (Ber., 1938, 71, [B], 1837—1842).—2-Methylchromone

(I) (modified prep. from HI and the Cu salt of *o*-methoxybenzoylacetone) is converted by the calc. amount of MnO₂ and HCl in boiling AcOH into 2-chloromethylchromone, m.p. 127°, in 60% yield. With MnO₂ (=3 mols.) and excess of HCl the product is a trichloro-2-methylchromone, m.p. 163° (yield 10%). Under varied conditions 2-bromomethylchromone, m.p. 117—118°, a dibromo-, m.p. 152°, and a tribromo-, m.p. 208—213°, -methylchromone are obtained by the rapid or slow action of Br on (I), the rapid or slow action of MnO₂ and HBr on (I), or from Br, MnO₂, and (I). With I in AcOH (I) gives only ill-defined products whereas in presence of MnO₂ 2-iodomethylchromone (II), m.p. 142° (decomp.), is produced. It is converted by molten PhOH and K₂CO₃ into 2-phenoxyethylchromone, m.p. 102° (yield 55%), and by AgNO₃ in EtOH into AgI and a very unstable substance, m.p. 155°. *o*-OH·C₆H₄·CO₂H is obtained by the action of alkali on the 2-monohalogenochromones. H. W.

Lower homologues of α-tocopherol. P. KARRER and H. FRITZSCHE (Helv. Chim. Acta, 1938, 21, 1234—1240).—Condensation of 2:5-dimethylquinol with phytol bromide (I) in boiling ligroin containing ZnCl₂ gives mainly the compound (II). In boiling C₆H₆ 3:5-dimethylquinol and (I) afford 5:7-dimethyltolcol (it is proposed to designate the unsubstituted structure A by the name tocol) and the



substance (III), isolated as the *allophanate*. 2:3-Dimethylquinol yields 6-hydroxy-2:7:8-trimethyl-2-δμ-trimethyltridecylchroman and the compound (IV). As variant of the above method the dimethylquinols can be condensed with phytol in boiling anhyd. HCO₂H in N₂. Thus are obtained non-cryst. 5:8-dimethyltolcol (*allophanate*, m.p. 139°) and 5:7-dimethyltolcol (*allophanate*). The synthetic compounds have pronounced vitamin-E activity. H. W.

Constitution and determination of α-tocopherol and similar compounds. P. KARRER, R. ESCHER, H. FRITZSCHE, H. KELLER, B. H. RINGLER, and H. SALOMON (Helv. Chim. Acta, 1938, 21, 939—953; cf. A., 1938, II, 374).—Trimethylquinol, crotyl bromide, and anhyd. ZnCl₂ in boiling light petroleum (b.p. 80—100°) give 6-hydroxy-2:5:7:8-tetramethylchroman (I), m.p. 143°. This can be determined by

titration in EtOH with FeCl_3 using KI-starch-AcOH paper as indicator or, better by potentiometric titration with FeCl_3 in 50% EtOH; $\text{AgNO}_3\text{-NH}_3$ may also be used potentiometrically. A third method consists in oxidation by $\text{Fe}(\text{CN})_6'''$ in presence of NaHCO_3 and measurement of the CO_2 evolved. When thus oxidised (I) affords 2 : 4 : 5-trimethyl-6- γ -hydroxy-butyl-p-benzoquinone, m.p. 52° , which gives CHI_3 when treated with I and alkali. It is reduced by Zn dust and AcOH to (I). The product obtained from allyl bromide (*loc. cit.*) is identified as 5-hydroxy-2 : 4 : 6 : 7-tetramethylcoumaran since oxidation with CrO_3 shows the presence of 4C-Me groups and oxidation with AuCl_3 yields 2 : 3 : 5-trimethyl-6- β -hydroxypropyl-p-benzoquinone, m.p. 56.5° , which gives CHI_3 with I and KOH. Coumaran and chroman compounds of analogous structure have nearly identical absorption spectra. For the determination of α -tocopherol (II), FeCl_3 and $\text{Fe}(\text{CN})_6'''$ are valueless but $\text{NH}_3\text{-AgNO}_3$ can be used; the most suitable oxidant is AuCl_3 . The product from synthetic (II) is a yellow liquid which contains 1 OH (Zerevitinov) and is regarded as 2 : 3 : 5-trimethyl-6- γ -hydroxy- γ - γ -tetramethylhexadecyl-p-benzoquinone, the *tert.* nature of OH being established by the absence of reaction with $\text{Al}(\text{OBu}^t)_3$. (I) has therefore the structure assigned to it by Fernholz (A., 1938, II, 186). Neotocopherol, allyl bromide, and ZnCl_2 yield allylneotocopherol (*allophanate*, m.p. 165°). *Crotylneotocopherol allophanate* has m.p. 142° . H. W.

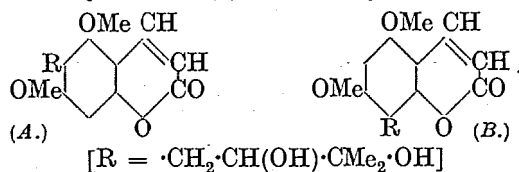
Vitamin-E. IV. Synthetic experiments in the coumarin and chroman series. Structure of the tocopherols. F. BERGEL, (MISS) A. JACOB, A. R. TODD, and T. S. WORK. V. Synthesis of racemic α -tocopherol and of a lower homologue. F. BERGEL, (MISS) A. M. COPPING, (MISS) A. JACOB, A. R. TODD, and T. S. WORK (J.C.S., 1938, 1375—1382, 1382—1384).—IV. Stearoyl chloride and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ give *Et stearoylacetoacetate*, m.p. 42° , which on gentle hydrolysis (NaOH) affords *Et stearoylacetate* (I), m.p. 46.5° , further hydrolysed to *Me n-heptadecyl ketone*, m.p. 57° (*semicarbazone*, m.p. $124\text{--}125^\circ$). ψ -Cumoquinone and (I) condense (Na) to 5-hydroxy-3-stearoyl-4 : 6 : 7-trimethylisocoumaranone (II), m.p. 104° , and small amounts of 5-hydroxy-4 : 6 : 7-trimethyl-2-n-heptadecylcoumarone (III), m.p. $101\text{--}102^\circ$, and the corresponding -3-carboxylic acid, m.p. $158\text{--}159^\circ$. The conversion of (II) into (III) can be carried out by heating with HCl-Zn (*Et* ester of the acid, m.p. $68\text{--}69^\circ$, also formed) or with HCl-Zn-AcOH . Reduction of (III) with H_2 (Pd-C) gives 5-hydroxy-4 : 6 : 7-trimethyl-2-n-heptadecylcoumaran, m.p. $95\text{--}95.5^\circ$ (*allophanate*, m.p. 192°), closely resembling the tocopherols in properties and pyrolysed to duroquinol. Similar reactions with *Et* palmitoylacetate afford 5-hydroxy-3-palmitoyl-4 : 6 : 7-trimethylisocoumaranone, m.p. 104° , 5-hydroxy-4 : 6 : 7-trimethyl-2-n-pentadecylcoumarone, m.p. $100\text{--}101^\circ$, and *Et* 5-hydroxy-4 : 6 : 7-trimethyl-2-n-pentadecylcoumarone-3-carboxylate, m.p. 63° . ψ -Cumoquinol is converted into O-monoallyl- ψ -cumoquinol, b.p. $110\text{--}120^\circ/0.5\text{ mm.}$, which when heated and treated with $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ gives 5-hydroxy-2 : 4 : 6 : 7-tetramethylcoumaran, m.p. $128\text{--}129^\circ$. *p*-Xyloquinol also forms

a monoallyl ether, b.p. $115\text{--}120^\circ/0.5\text{ mm.}$ 6-Acetoxy-4-methylcoumarin and MgMeI afford 6-hydroxy-2 : 2 : 4-trimethyl- Δ^3 -chromen, m.p. $104\text{--}105^\circ$, reduced ($\text{H}_2\text{-Pd-C}$) to the -chroman, m.p. $107\text{--}108^\circ$, which also closely resembles the tocopherols in reducing properties and absorption spectra. Oxidation of β -tocopherol with CrO_3 gives a small amount of acid, $\text{C}_{12}\text{H}_{24}\text{O}_2$.

V. Phytol and ψ -cumoquinol condense (ZnCl_2) to racemic α -tocopherol; the method does not distinguish between alternative formulæ (cf. Karrer *et al.*, A., 1938, II, 290). Phytol and *m*-xyloquinol similarly afford a product of high vitamin-E activity (*allophanate*, m.p. $148\text{--}149^\circ$). F. R. S.

Synthesis of 5-hydroxycoumarin. H. A. SHAH and R. C. SHAH (Current Sci., 1938, 7, 107—108).—Me 2-hydroxy-3-aldehydo-4-methoxybenzoate with $\text{CH}_2(\text{CO}_2\text{Et})_2$ gives *Et Me 5-methoxycoumarin-3 : 8-dicarboxylate*, m.p. $186\text{--}188^\circ$, hydrolysed to the acid, m.p. 281° , which when decarboxylated and demethylated gives 5-methoxy-, m.p. $85\text{--}87^\circ$, and 5-hydroxy-coumarin, m.p. $221\text{--}223^\circ$. A. LI.

Natural coumarins. XLI. Constitution of toddalolactone. E. SPÄTH, B. B. DAY, and E. TYRAN (Ber., 1938, 71, [B], 1825—1830; cf. Dey and Pillay, A., 1934, 88).—Toddalolactone (I) is converted by $\text{Pb}(\text{OAc})_4$ in C_6H_6 into COMe_2 and an aldehyde, $\text{C}_{13}\text{H}_{12}\text{O}_5\cdot\text{MeOH}$, m.p. $142\text{--}142.5^\circ$ (vac.); the side-chain therefore is $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2$. Me_2SO_4 , NaOH , and (I) afford a methoxylated cinnamic acid, converted by energetic oxidation into 2 : 4 : 6 : 1 : 3-(OMe) $_3\text{C}_6\text{H}(\text{CO}_2\text{H})_2$. (I) is therefore A or B. Ethylation of (I) followed by oxidation of the



product and subsequent methylation gives a product (II), m.p. $89\text{--}90.5^\circ$; this is also obtained by transforming 2 : 4 : 6 : 1 : 3-(OH) $_3\text{C}_6\text{H}(\text{CO}_2\text{Et})_2$ into its *Et* ether, m.p. $128\text{--}130^\circ$ (vac.), which is then treated with CH_2N_2 , hydrolysed, and again treated with CH_2N_2 . This is presumably *Me* $_2$ 4 : 6-dimethoxy-6-ethoxybenzene-1 : 3-dicarboxylate, indicating the structure A for (I). Further proof of the constitution of (II) is regarded as desirable. H. W.

Natural coumarins. XLII. Syntheses of fraxetin, fraxidin, and isofraxidin. E. SPÄTH and E. DOBROVOLNY (Ber., 1938, 71, [B], 1831—1836).—4-Nitropyrogallol is treated with the amount of CH_2N_2 required for reaction with one OH and the product after purification yields a homogeneous 4-nitropyrogallol 1-(or 2-)Me ether, m.p. $127\text{--}128^\circ$, not identical with the 4-nitropyrogallol 3-Me ether, m.p. $122\text{--}123^\circ$, obtained from the corresponding 1 : 2-carbonate. 2 : 3 : 4 : 5-(OH) $_4\text{C}_6\text{H}\cdot\text{CHO}$ condenses with $\text{CH}_2(\text{CO}_2\text{H})_2$ in presence of $\text{C}_5\text{H}_5\text{N}\cdot\text{NH}_2\text{Ph}$ to 6 : 7 : 8-trihydroxycoumarin-3-carboxylic acid, m.p. $246\text{--}248^\circ$ (vac.), decarboxylated to 6 : 7 : 8-trihydroxycoumarin, m.p. $270\text{--}272^\circ$ (vac.). Scopoletin in AcOH is nitrated to 3-nitroscopoletin,

reduced ($\text{Na}_2\text{S}_2\text{O}_4\text{--NaOH}$) to 3-aminoscopoletin, m.p. 195—197°; the corresponding Me_2 ether, m.p. 175—177° (vac.), is converted by 5% HCl at 150° into 3-hydroxyscopoletin, m.p. 260—263°, methylated to 3:6:7-trimethoxycoumarin (I), m.p. 146—148° (vac.). Æsculetin Me_2 ether gives (fuming HNO_3 in AcOH) 3-nitroæsculetin Me_2 ether, m.p. 256—259° (vac.; decomp.), reduced (conc. HCl , SnCl_2 , and a little pptd. Sn at 50°) to 3-aminoæsculetin Me_2 ether, m.p. 183—184° (vac.), whence 3-hydroxyæsculetin Me_2 ether, m.p. 222—223° (vac.), transformed by an excess of CH_2N_2 into (I). 2:3-Dihydroxy-4-methoxybenzaldehyde, m.p. 117—118°, is converted by H_2O_2 and NaOH into apionol 1-Me ether (2:3:4-hydroxy-anisole), m.p. 116—117°. This condenses with Et sodioformylacetate at 25°, giving fraxetin (II), m.p. 230—232°. Since the transformations of (II) into fraxidin and isofraxidin are partial syntheses, the prep. of (II) gives the bridge to the syntheses of these natural coumarins.

H. W.

Pechmann's condensation of methyl β -resorcylicate with ethyl α -alkylacetoacetates. S. M. SETHNA and R. C. SHAH (J. Indian Chem. Soc., 1938, 15, 383—388).—Me β -resorcylicate, $\text{CHMeAc}\cdot\text{CO}_2\text{Et}$, and 80% H_2SO_4 at room temp. give 7-hydroxy-3:4-dimethylcoumarin-6-carboxylic acid, $+\text{H}_2\text{O}$, m.p. 263°, and its Me ester, m.p. 212—213° (Ac , m.p. 178—180°, and Bz derivative, m.p. 159—160°; Me ether, m.p. 185—187°). With HCl at 180—190° or alone at 265—270° the acid gives 7-hydroxy-3:4-dimethylcoumarin. Similarly are obtained 7-hydroxy-4-methyl-3-ethyl-, m.p. 243—245° [Me ester, m.p. 144—146° (Ac derivative, m.p. 146—147°)], -3-propyl-, m.p. 230—231° [Me ester, m.p. 142—144° (Me ether, m.p. 138—140°), purified by way of the Ac derivative, m.p. 113°], -3-butyl-, m.p. 222° [Me ester, m.p. 163—165° (Ac derivative, m.p. 111—113°; Me ether, m.p. 150—152°)], and -3-benzylcoumarin-6-carboxylic acid, m.p. 247—248° [Me ester, m.p. 186—188° (Me ether, m.p. 146—148°; Ac derivative, m.p. 132—134°)], 7-hydroxy-4-methyl-3-ethyl-, m.p. 196—197°, -3-propyl-, m.p. 171—173°, and -3-butylcoumarin, m.p. 134—136° (also obtained from $\text{CHBu}^a\text{Ac}\cdot\text{CO}_2\text{Et}$, resorcinol, and 80% H_2SO_4). β -Resorcylic acid could not be condensed with $\text{CHMeAc}\cdot\text{CO}_2\text{Et}$.

R. S. C.

Preparation of flavones from o-aroxyloxyacetophenones. V. V. VIRKAR and T. S. WHEELER (Current Sci., 1938, 7, 107; cf. A., 1933, 1301, and Bhalla *et al.*, A., 1935, 1129).—Flavones and 2-alkylchromones have been prepared by the rearrangement of o-aroxy- and -acyl-oxyacetophenones respectively, using Na in Et_2O or PhMe .

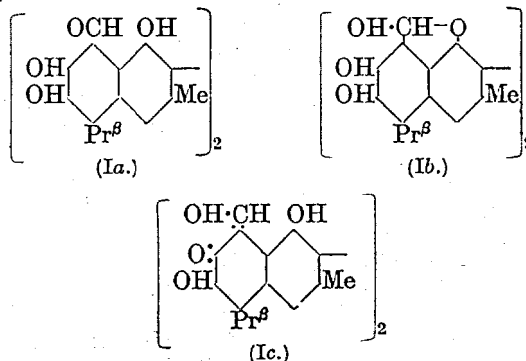
A. Li.

Chalkones. Condensation of aromatic aldehydes with resacetophenone. II. D. R. NADKARNI and T. S. WHEELER (J.C.S., 1938, 1320—1322; cf. A., 1938, II, 18).— $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, resacetophenone (I), and aq. $\text{EtOH}\text{--KOH}$, when kept at room temp. out of contact with air for 2 days, yield 2:4-dihydroxyphenyl p -methoxystyryl ketone, m.p. 194° (lit., 186°), which with SeO_2 and $\text{C}_5\text{H}_{11}\cdot\text{OH}$ (150°; 12 hr.) gives 7-hydroxy-4'-methoxyflavone (pratol), with H_2O_2 in $\text{EtOH}\text{--KOH}$ gives 7-hydroxy-4'-methoxyflavonol (resokaempferide), m.p. 286—288° (lit., 284°), and on bromination gives 3:5-dibromo-

2:4-dihydroxyphenyl $\alpha\beta$ -dibromo- β - p -anisylethyl ketone, m.p. 182—184°. This with $\text{KOH}\text{--H}_2\text{O}\text{--COMe}_2$ in the cold, or with boiling COMe_2 , gives 6:8-dibromo-7-hydroxy-4'-methoxyflavone, m.p. 194°. Similarly, $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and (I) give 2:4-dihydroxyphenyl p -hydroxystyryl ketone (II) as the monohydrate, m.p. 202—204° (cf. lit.), also obtained on repetition of Tambor's method (A., 1916, i, 831), and converted by aq. $\text{EtOH}\text{--NaOH}$ at the b.p. (6 hr.) into 7:4'-dihydroxyflavanone (liquiritigenin). This and (II) are obtained on hydrolysis of the Ac_3 derivative of (II) with aq. KOH (cf. Russell *et al.*, A., 1937, II, 206).

H. G. M.

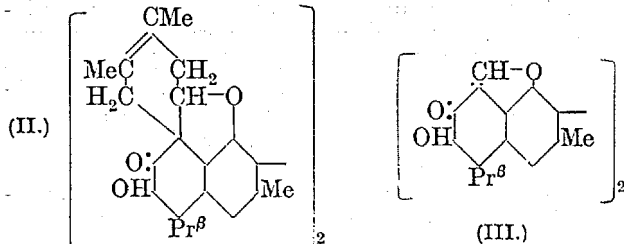
Structure of gossypol. V. Anilino-derivatives. R. ADAMS, C. C. PRICE, and W. R. DIAL. VI. Addition products with butadienes. R. ADAMS, B. S. FRIEDMAN, C. C. PRICE, R. C. MORRIS, and E. C. KIRKPATRICK. VII. Gossypol dimethyl ether. VIII. Derivatives of the ethers of gossypol. R. ADAMS and T. A. GEISSMAN. IX. Oxidation and degradation of gossypol hexamethyl ether; gossic acid. R. ADAMS, R. C. MORRIS, and E. C. KIRKPATRICK. X. apoGossypol and its degradation products. R. ADAMS and D. J. BUTTERBAUGH. XI. Absorption spectra of gossypol, its derivatives, and of certain dinaphthalene compounds. R. ADAMS and E. C. KIRKPATRICK. XII. Gossylic acid lactone tetramethyl ether. R. ADAMS and T. A. GEISSMAN. XIII. Conversion of gossic acid to apogossypolic acid. R. ADAMS and R. C. MORRIS. XIV. apoGossypolic acid. R. ADAMS, R. C. MORRIS, D. J. BUTTERBAUGH, and E. C. KIRKPATRICK. XV. Interpretation of its reactions. R. ADAMS, R. C. MORRIS, T. A. GEISSMAN, D. J. BUTTERBAUGH, and E. C. KIRKPATRICK (J. Amer. Chem. Soc., 1938, 60, 2158—2160, 2160—2162, 2163—2166, 2166—2170, 2170—2174, 2174—2180, 2180—2184, 2184—2188, 2188—2190, 2191—2193, 2193—2204; cf. A., 1937, II, 463).—The detailed formulæ given below are developed later and are based on gossypol being tautomeric, (Ia), (Ib); and (Ic).



V. The symmetry of (I) is indicated by its invariably reacting with 2 mols. of reagent, *e.g.*, with bases. Contrary to Karrer and Tobler (A., 1932, 1256) it condenses with 2 mols. of $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in CHCl_3 , giving di-o-aminoanilinogossypol, stable, m.p. 246°, and unstable form, m.p. 184°. Di- β -naphthylamino-gossypol, m.p. 310—313° (decomp.) [hydrolysed by H_2SO_4 to (I)], is prepared, but the products from 5

other bases, though hydrolysed to (I), could not be purified. Generally the Ac derivatives of the products could not be purified, but dianilnogossypol affords the Ac_6 derivative, m.p. 185°, decomp. 220° giving NHPAc; similarly, when it is heated with Me_2SO_4 and C_6H_5N in $CHCl_3$, *dimethyl dianilnogossypol*, m.p. 253—258° (stable to conc. H_2SO_4 and not containing OMe), is formed, although, when kept at room temp., an unintelligible reaction leads to *dimethyl dianilino-oxogossypol*, $C_{44}H_{42}O_7N_2$, m.p. 275—280° (unchanged by conc. H_2SO_4). The basic compounds are thus formed by reaction of the OH of a $CO\cdot CH\cdot CH\cdot OH$; they are tautomeric, reacting either as the anil etc. of (Ia) or as (Ib) or (Ic) in which the OH is replaced by $NHAr$; methylation and acylation occur on the N, thus stabilising the product in b or c form. Zeisel determinations show absence of OMe in (I).

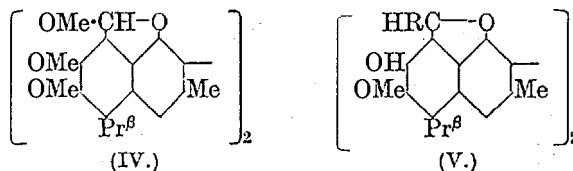
VI. The presence of $CO\cdot CH\cdot CH\cdot OH$ in (I) and its derivatives is confirmed by diene addition. Thus, (I) and $(CH_2\cdot CMe)_2$ (2 mols.) in abs. EtOH or C_6H_6 give the *adduct* (II), $C_{42}H_{46}O_6$, m.p. 244—245° (decomp.) [red $FeCl_3$ colour; Ac_2 derivative, m.p. 227—



229°, hydrolysed to (II); Me_2 ether, m.p. 227—229°, obtained by Me_2SO_4 —30% KOH—MeOH; stable to 40% aq. NaOH; resists H_2 —PtO₂—Pd-black; decomposed when kept in H_2SO_4 , 2 H_2O being eliminated. (II) is also obtained from anhydrogossypol (III) by simple addition without elimination of H_2O and from diaminogossypol by loss of 2 NH_3 . The structures postulated for the O rings account for the ready conversion of (III) into (I) and its derivatives, contrasted with the stability of (II). The *o*-hydroxyketone structure of (II) is proved by its giving a red colour with Na pyroboracetate. The fact that (III) and liquid NH_3 give diaminogossypol and not a N-ring compound indicates that the OH *peri* to the CHO is phenolic. The ease of the above diene additions and the failure of the reaction with gossypol Me_6 and Me_4 ethers and hexa-acetate indicate a structure $C\cdot CH\cdot OH$, rather than $C\cdot CR\cdot OH$ (i.e., CHO and not COR), and also exclude other possible structures. $(CH_2\cdot CH)_2$ and (III) in C_6H_6 give an *adduct*, m.p. 245—246° (decomp. from 242°) [Ac_2 derivative, m.p. 250—251° (decomp.)], which dissociates when kept in C_6H_6 .

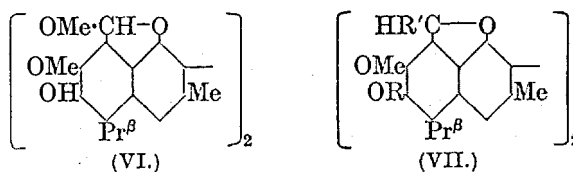
VII. The white (IV) or red gossypol Me_6 ether with a little H_2SO_4 in AcOH at 100° gives *gossypol Me_2 ether* [(V), $R = OH$], m.p. (anhyd.) variable, 230—232° (decomp.), and (+AcOH) about 155—165° (decomp.), which gives orange-red colours with H_2SO_4 or $SnCl_4$ and a green colour with $FeCl_3$. With NH_2Ph in hot C_6H_6 the Me_2 ether gives the *dianilino-compound* [(V), $R = NHPH$], m.p. 268—270° (decomp.), which with a trace of HCl in AcOH regener-

ates the Me_2 ether. Gossypol Et_6 ether gives a similar *Et₂ ether*, m.p. 193—195° (decomp.). With

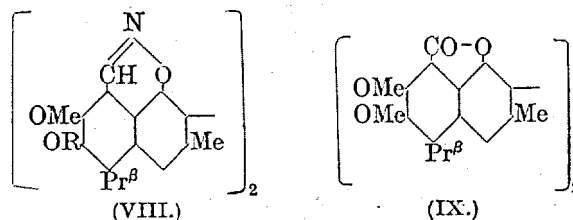


Me_2SO_4 —KOH—MeOH the Me_2 ether gives the form, m.p. 225°, of (IV). Prep. of white gossypol Me_6 ethers (IV) in three forms, two (m.p. 216—218° and 224—225°) dimorphic and one [m.p. 240° (lit. 235°)] different, is modified; the exact relation of these stereoisomerides is unknown, but they give the same reaction products. Oxidation of the Me_2 ether by air in warm 25% aq. NaOH gives a *substance*, $C_{30}H_{30}O_8$, m.p. 246° (decomp.), and by $FeCl_3$ in hot AcOH or by dil. HNO_3 (1:4) gives a *substance*, $C_{32}H_{30}O_{10}$, m.p. 215—216°. M.p. are corr.

VIII. Although stable to neutral and alkaline reagents, gossypol Me_6 (IV) and Me_4 ethers (VI) react with bases in AcOH with elimination of 2 OMe. Further, $KMnO_4$ —AcOH oxidises (IV), although no products could be isolated. $NHPh\cdot NH_2$ and (IV) (forms, m.p. 240° or 225°) in AcOH give the *product*



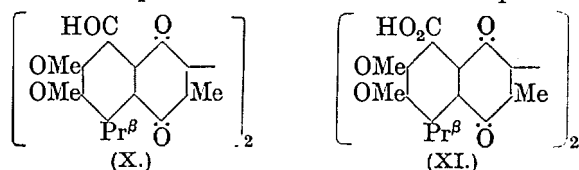
[(VII), $R = Me$, $R' = NHPH\cdot NH$], m.p. 266—267° (decomp.), which with HCl—AcOH gives a *Cl-compound*, m.p. 257—262° (decomp.), converted by HCl—MeOH into a *Cl-compound*, m.p. 274—276° (decomp.). With HCl—MeOH at room temp. [(VII), $R = Me$, $R' = NHPH\cdot NH$] regenerates the Me_6 ether (IV) and with HCl—EtOH gives *gossypol Me_4 Et₂ ether* [(VII), $R = Me$, $R' = OEt$], m.p. 229—230°. Similarly, (VI) and $NHPh\cdot NH_2$ in AcOH give the *substance* [(VII), $R = H$, $R' = NHPH\cdot NH$], m.p. 246—248° (decomp.), converted by HCl—MeOH into (VI) and by HCl—EtOH into *gossypol Me_2 Et₂ ether* [(VII), $R = H$, $R' = OEt$], m.p. 160—162°. With NH_2OH in AcOH at 100° 2 H_2O (as well as 2 OMe) are eliminated: (IV) gives the *orthoxazine compound* [(VIII),



$R = Me$], dimorphic, m.p. 192—204° (rapid heating) or >280° (slow heating), converted by hot 10% KOH—MeOH into the K_2 salt (type $X < \begin{smallmatrix} O \\ CH\cdot NO \end{smallmatrix} K$), which with AcOH gives a *cryst. product* and thence by hot Ac_2O *gossylolactone Me_4 ether* (IX), m.p. 327—328°; intermediates of the types, $OH\cdot X\cdot CN$ and

$X < \begin{smallmatrix} \text{O} \\ \text{C} \end{smallmatrix} \text{NH}$, are postulated. Similarly the Me_4 ether (VI) gives the compound [(VIII), $\text{R} = \text{H}$], m.p. 281—283° (decomp.). The Me_2 ether [(V), $\text{R} = \text{OH}$] condenses normally giving a di(phenylhydrazino)-derivative [(V), $\text{R} = \text{NHPh} \cdot \text{NH}$], m.p. 248—249° (decomp.), and a dioxime, m.p. 229—232°. M.p. are corr.

IX. The white Me_6 ether (IV) gives cryst. oxidation products, but the Me_4 ether gives only H_2O -sol. acids. Short treatment of (IV) or of gossypol $\text{Me}_4 \text{Et}_2$ ether in boiling AcOH with aq. CrO_3 or, much less well, HIO_4 oxidation of (IV) gives gossypolone Me_4 ether (X), $\text{C}_{30}\text{H}_{22}\text{O}_6(\text{OMe})_4$, m.p. 156—157° (red colour with Na pyroborate, none with FeCl_3 ; insol. in aq. KOH ; decomposed by $\text{KOH}-\text{MeOH}$), and a small amount of the lactone (IX). Presence of 2 CHO in (X) is indicated by formation of a dianil, m.p. 213—215°, and absence of CO_2H by electrometric titration; a quinone structure is considered probable.



With hot $\text{HNO}_3-\text{H}_2\text{O}$ (1 : 4) (IV) gives gossypolonic acid Me_4 ether (XI), $\text{C}_{30}\text{H}_{22}\text{O}_8(\text{OMe})_4$, m.p. 249—251° (decomp.) [also obtained from (X) by HNO_3], and gossic acid [6-carboxy-4 : 5-dimethoxy-3-isopropylphthalic anhydride] (XII), m.p. 184—186° [also obtained from (X) or (XI) by KMnO_4 ; tribasic in H_2O , but with CH_2N_2 gives a Me_1 ester, m.p. 106°, hydrolysed to (XII) by 10% NaOH]. With 100% HNO_3 (XI) and (IV) give cryst. products. With NH_3 in $\text{H}_2\text{O}-\text{COMe}_2-\text{EtOH}$ (X) gives a substance, m.p. $>300^\circ$.

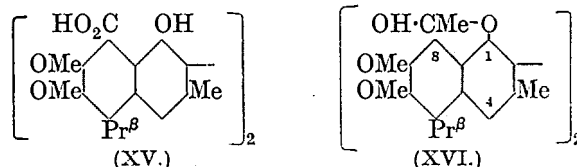
X. apoGossypol (modified prep.; cf. Clark, A., 1932, 1016) is formed from gossypol by loss of CO and is thus (Ia) without the CHO. It gives Ac_4 , m.p. 230—232°, and Bz_4 derivatives, m.p. 314—316° (cf. loc. cit.). Tetramethoxy- β -gossypolone, obtained from apogossypol Me_6 ether (XIII) by CrO_3 (loc. cit.) or HIO_4 in aq. dioxan, is renamed apogossypolone Me_4 ether [(X) without CHO], and tetra-acetyl-apogossypolone is the corresponding tetra-acetate, $\text{C}_{28}\text{H}_{22}\text{O}_4(\text{OAc})_4$ [lit. $\text{C}_{22}\text{H}_{16}\text{O}_2(\text{OAc})_4$]. The quinone nature of these substances is proved by reductive acetylation to hydroapogossypolone octa-acetate, m.p. 225—229° (reconverted into the quinone tetra-acetate by CrO_3), and hydroapogossypolone Me_4 ether tetra-acetate, m.p. 229—230.5°. apoGossypolic acid [4 : 5-dimethoxy-3-isopropylphthalic acid] (XIV) (prep. described), $\text{C}_{13}\text{H}_{16}\text{O}_6$ (Clark, $\text{C}_{20}\text{H}_{24}\text{O}_9$), m.p. variable, 162—165°, gives a Me_2 ester, m.p. 45—46.5°, and at 170—180°/25 mm. an anhydride, m.p. 93—94° (Clark, 95°), which with $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ gives a compound, m.p. 221—223° (Clark, 233°), of the type, $X < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$. When kept in conc. H_2SO_4

at room temp. for 15 min., (XIII) loses 2 C_3H_6 and yields de-apogossypol Me_6 ether [di-(1 : 6 : 7-trimethoxy-3-methyl-2-naphthyl)], m.p. 295—296°, converted by HIO_4 (not CrO_3) into de-apogossypolone Me_4 ether [di-6 : 7-dimethoxy-3-methylnaphtha-1 : 4-

quinonyl], m.p. 245—248° (decomp.), which (a) is proved to be a quinone by reductive acetylation to hydrode-apogossypolone Me_4 ether tetra-acetate, m.p. 264—266° [reoxidised by HIO_4], and (b) is converted by KMnO_4 at 0° into 4 : 5 : 1 : 2-(OMe) $_2\text{C}_6\text{H}_2(\text{CO}_2\text{H})_2$, identified as anhydride, acid, and N-ethylimide. In the conversion of the apo- into the de-apo-series the 2 C_3H_6 are probably lost as Pr^βOH ; COMe_2 was identified by a ppt. formed after treating the acid reaction mixture with $\text{K}_2\text{Cr}_2\text{O}_7-\text{HgSO}_4$. The presence of Pr^β in gossypol is thus indicated. apoGossypol Et_6 ether, m.p. 176—180°, did not yield a de-apo-compound. Gossypol Me_2 ether and 30% $\text{KOH}-\text{MeOH}$ in N_2 at 100° give an amorphous ether, converted by alkaline methylation into (XIII). The similarity of the apo- and de-apo-series is stressed. The OMe and quinone groups of the "olone" compounds are in different rings, the quinone groups yielding the 2 CO_2H of hemipinic and apogossypolic acid. The Pr must be in the ring containing the OMe.

XI. Absorption spectra confirm the chemical findings. The intense absorption [max. at about 2500 Å. ($\log \epsilon$ about 5); point of inflexion near 3000 Å. ($\log \epsilon$ 4)] of gossypol (I) and its closely related derivatives necessitates aromatic structure. Of known aromatic and O-ring compounds, including quinones, only $(\text{C}_{10}\text{H}_7)_2$ compounds are similar. (α - and β - C_{10}H_7) $_2$ are most similar. Tautomerism is indicated by absorption max. at 3600 Å. for (I) and its Me_2 ether [(V), $\text{R} = \text{OH}$], but not for the Me_6 or Me_4 ether or hexa-acetate. Corresponding gossypol, apo- and de-apo-gossypol derivatives have very similar absorption, proving the differences to lie only in the substituents. The quinones ("olone" compounds) have the anticipated absorption of different type (max. near 2500 Å.), reconverted into the gossypol type by reductive acetylation. Anhydrogossypol (III) has a triple-banded max. at about 2700 Å., indicating a deep-seated change, e.g., of ring structure with unsaturation.

XII. Gossylic lactone Me_4 ether (IX) is shown, mainly by the reaction with CH_2N_2 , to be a dilactone of CO_2H with phenolic OH in the peri positions of C_{10}H_8 nuclei, and by reactions marked * to contain a substituent ortho to the CO_2H . With 10% $\text{KOH}-\text{MeOH}-\text{H}_2\text{O}$ and a little Zn dust (IX) gives gossylic acid Me_4 ether (XV), m.p. 290° (loss of H_2O and re-solidification), converted by $\text{Me}_2\text{SO}_4-10\%$ $\text{KOH}-\text{MeOH}$ or by CH_2N_2 into Me_2 gossylate Me_6 ether, m.p. 215—216.5° (resists hydrolysis*). With MgMeI (1



mol. or an excess*) (IX) gives homogossypol Me_4 ether (XVI), m.p. 308—309° (decomp.; corr.) (MgPhBr , however, gives only oils), which with $\text{Me}_2\text{SO}_4-30\%$ $\text{KOH}-\text{EtOH}$ gives the ether, 8-COMe-X-OMe-1, m.p. 242—243° (corr.), and with $\text{MeOH}-\text{H}_2\text{SO}_4$ or an excess of Me_2SO_4 in alkali gives the ether,

$1 > X < \begin{smallmatrix} \text{O} \\ \text{CMe} \cdot \text{OMe} \end{smallmatrix}$, m.p. 255—256°. The lactone (IX)

resists reduction and is either completely or not at all oxidised; however, the acid (XIV) with 1:4 $\text{HNO}_3\text{-H}_2\text{O}$ gives the quinone (XI). All the quinones of the gossypol and apogossypol series are yellow and thus probably *p*-quinones; it follows that position 4 must be unsubstituted. With $\text{HNO}_3\text{-AcOH}$ (IX) gives 4:4'-dinitrogossylolactone Me_4 ether, double m.p. 238—239° and 247—248° or only 247—248°, reduced (Zn-AcOH , $\text{Na}_2\text{S}_2\text{O}_4$, or Fe-AcOH) to the $(\text{NH}_2)_2$ -derivative, m.p. 293—294° (decomp.; corr.) [Ac_2 derivative, m.p. 252—253° (corr.)]. Acid- MeOH^* or Ac_2O lactonises (XV).

XIII. Gossic acid (XII) is hydrolysed by warm 10% NaOH to a tribasic acid, which could not be isolated, but yields (CH_2N_2) a Me_3 ester [Me_3 4:5-dimethoxy-6-isopropylhemimellitate], m.p. 70—71°. Demethylation of (XII) by HBr gives an acid [4:5-dihydroxy-3-carboxy-6-isopropylphthalic anhydride] (XVII), m.p. 140—141° (CH_2N_2 gives *Me* gossate), decarboxylated by Cu -bronze in quinoline at 160—165° to give a product [4:5-dihydroxy-3-isopropylphthalic anhydride] (XVIII), m.p. 165—166°, which with CH_2N_2 gives apogossypolic anhydride. (XVII) and (XVIII) give green FeCl_3 colours, indicating presence of *o*-(OH)₂, and with air in alkali give a red quinone, $\text{C}_9\text{H}_{10}\text{O}_4$, m.p. 179—181° (reduced by $\text{Na}_2\text{S}_2\text{O}_4$ and then reoxidised by air).

XIV. apogossypolic acid (XIV) is probably 4:5:3:1:2-(OMe)₂ $\text{C}_6\text{HPr}^a(\text{CO}_2\text{H})_2$ rather than 4:5:1:2-(OMe)₂ $\text{C}_6\text{H}_2(\text{CO}_2\text{H})\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ (A) (the only alternative). With HBr it gives a monocarboxylic acid, $\text{C}_{16}\text{H}_{12}\text{O}_4$, m.p. 216—217° (green FeCl_3 colour), which is 3:4-dihydroxy-2-isopropylbenzoic acid rather than 3:4-(OMe)₂ $\text{C}_6\text{H}_3\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ [derived from (A)], because with CH_2N_2 it readily gives the ester [Me 3:4-dimethoxy-2-isopropylbenzoate], m.p. 106—107°, which is readily hydrolysed by 10% NaOH to the corresponding acid, m.p. 167—169° (resists oxidation), the absorption spectrum of which resembles that of veratric and differs from that of homoveratric acid. Further, with 1:3 $\text{HNO}_3\text{-H}_2\text{O}$ (XIV) exchanges a CO_2H for NO_2 , giving 6-nitro-3:4-dimethoxy-2-isopropylbenzoic acid, m.p. 155—158°, which is hydrogenated (Raney Ni ; 2.5 atm.) to the NH_2 -acid, m.p. 74—76° (*Ac* derivative, m.p. 85—86°); the corresponding product from (A) would have been a lactam, $(\text{OMe})_2\text{C}_6\text{H}_4\langle\text{NH}\rangle\text{CO}$. The structures given earlier for gossic acid and (XIV) follow.

XV. The reactions described above and earlier are shown to be best explained by the structures given. An alternative structure based on $(\text{C}_{10}\text{H}_7\cdot\text{CH}_2)_2$ for gossypol is improbable, since much AcOH , but no $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, is obtained on oxidation. The Pr^a (rather than Pr^e) is supported by the formation of $\text{Pr}^a\text{CO}_2\text{H}$. The 3- rather than the 2-position of the *Me* is preferred by analogy with other products. (I) is composed of six isoprene units. A few reactions and derivatives still await explanation. R. S. C.

Rottlerin. II. K. S. NARANG, J. N. RAY, and B. S. ROY (J. Indian Chem. Soc., 1938, 15, 393—398).—Facts and views already reported (A., 1938, II, 66, 151, 199, 373) are given in greater detail. The following is new. The N_2O_3 adduct (I) of rottlerin

Me_5 ether is insol. in alkali and gives no FeCl_3 colour, but with NaOH in hot aq. EtOH yields an alkali-sol. "isonitrosite" (II), m.p. 153°, giving a violet FeCl_3 colour and reduced by $\text{H}_2\text{-Pt}$ to an alkali-sol. "dihydroisonitrosite" (III), m.p. 139° (violet FeCl_3 colour), also obtained from the H_2 -derivative of (I) and NaOH . The substance obtained from (III) by KMnO_4 is $\text{C}_{26}\text{H}_{29}\text{O}_8\text{N}$ and has m.p. 124°. The same *Me* or Me_2 ether, m.p. 192—193°, is obtained from (I) or (II) by $\text{Me}_2\text{SO}_4\text{-NaOH}$. The product, $\text{C}_{20}\text{H}_{22}\text{O}_4$, m.p. 171° (*ibid.*, 66) is proved to be tetrahydro-rottlerin by methylation to dimethyldihydrorottlerinone. Formation of the "isonitrosites" probably involves fission of the chroman ring. R. S. C.

Xanthones.—See B., 1938, 1136.

Attempts towards the synthesis of cantharidin.

II. P. C. GUHA and B. H. IYER (J. Indian Inst. Sci., 1938, 21, A, 115—118).— $(\text{CO}_2\text{Et}\cdot\text{CH}_2)_2\text{O}$ and $\text{Et}_2\text{C}_2\text{O}_4$ with NaOEt in EtOH yield Et_2 oxalodiglycollate, the Na_2 derivative of which with $(\text{CH}_2\text{Br})_2$ at 130—140° gives a compound, m.p. 174—175°, probably $\text{CH}_2\cdot\text{O}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{O}$, since it gives no semicarbazone and is hydrolysed to an acid, $\text{C}_8\text{H}_6\text{O}_7$, m.p. 316° (decomp.), which could not be decarboxylated. $\text{Br}\cdot[\text{CH}_2]_3\cdot\text{Br}$ gives an analogous compound (poor yield), m.p. 139°, whilst the Na_2 derivative of Et_2 oxalothiodiglycollate with $(\text{CH}_2\text{Br})_2$ yields the corresponding thio-compound, m.p. 148—150°. A. LI.

Indigoid dyes. III. S. K. GUHA (J. Indian Chem. Soc., 1938, 15, 359—364; cf. A., 1937, II, 393).—2-Hydroxy-3-methylthionaphthen (I), glyoxal *H* sulphite, and conc. HCl in EtOH give "bis-4-methyl-2-thionaphthenethyleneindigo" [α -di-2-keto-3-methyldihydro-1-thionaphthenylidene-ethane], m.p. >312°. "Bis-2-thionaphthenethyleneindigo," m.p. 303° (decomp.), is similarly prepared. With the appropriate aldehyde (I) gives 2-keto-1-benzylidene-, m.p. 132°, -1-*p*-nitro-, m.p. 273°, and -1-*p*-dimethylamino-benzylidene-4-methyldihydrothionaphthen-, m.p. 202°. Aceanthraquinone, 2-hydroxy-3- and -5-methylthionaphthen, and conc. HCl in AcOH give 3-, m.p. >305°, and 5-methyl-1:8'-thionaphthenace-naphthenylindigo, cryst. (cf. A., 1936, 861 for nomenclature). The effect of *Me p*- to the *S* on the absorption spectrum and shades dyed on wool and cotton is intermediate between its effects when in the two *m*-positions. R. S. C.

Oxidation of aqueous solutions of dyes.—See A., 1938, I, 525.

Pyrrolinium bases. R. LUKEŠ and J. PŘEVŮČIL (Coll. Czech. Chem. Comm., 1938, 10, 384—397).—1:1-Dimethylpyrrolidinium hydroxide is decomposed by heat to δ -dimethylamino- Δ^a -butene (I) and δ -dimethylaminobutanol, m.p. 187° (methiodide, m.p. 134°; hydrochloride of *Bz* derivative, m.p. 106—108°) (cf. Ciamician *et al.*, A., 1885, 1242). (I) and Br in CHCl_3 or HBr-Br give α -dibromo- δ -dimethylaminobutane hydrobromide (II), m.p. 191°, a suspension in C_6H_6 being converted by NaOH into 3-bromo-1:1-dimethylpyrrolidinium bromide (III), m.p. 194°, also obtained from 1:1-dimethyl- Δ^3 -pyrrolinium bromide, m.p. 288°, and excess of HBr in a sealed tube at

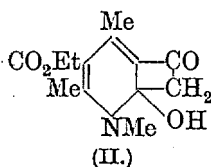
80—90° for 3—4 hr. (II) or (III) and Ag_2O afford 1:1-dimethyl- Δ^2 -pyrrolinium hydroxide (IV) (bromide, m.p. 231°; iodide, decomp. 200—210°; perchlorate, explodes at 270°); the acetate is decomposed in presence of AcOH to give NHMe_2 , no 1-methyl- Δ^2 -pyrroline being identified. Distillation of the formate corresponding with (IV) yields 1-methylpyrrolidine, whereas the Δ^3 -isomeric formate gives 1-methyl- Δ^3 -pyrroline. A. T. P.

Silver salt and nitrophenylhydrazone, m.p. 151°, of 2-pyrrol isobutyl ketone.—See A., 1938, III, 942.

4-Acetylpiperidine. V. PRELOG (Coll. Czech. Chem. Comm., 1938, 10, 380—383).—Et piperidine-4-carboxylate (cf. Clemo and Metcalfe, A., 1937, II, 466) in CHCl_3 , K_2CO_3 , a little H_2O , and BzCl , yield the *N*-Bz derivative (I), m.p. 76—77°, which with NaOMe - EtOAc - C_6H_6 gives impure Et β -keto- β -*N*-benzoyl-4-piperidylpropionate, hydrolysed (aq. HCl) to 4-acetylpiperidine (hydrochloride, m.p. 156—157°; platinichloride, m.p. 187°; picrate, m.p. 163.5°). (I) and NaOMe at 130° afford EtOBz, BzOH , and a compound hydrolysed by aq. HCl (1:1) to BzOH and piperidine-4-carboxylic acid. A. T. P.

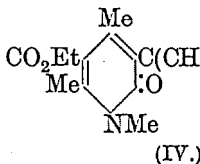
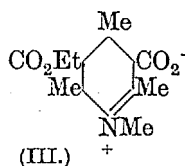
Derivatives of pyridine-3-sulphonic acid. G. MACHEK (Monatsh., 1938, 72, 77—92).— $\text{C}_5\text{H}_5\text{N}$ and oleum (20% SO_3) (+ HgSO_4) at 230° for 12—14 hr. yield 3- $\text{C}_5\text{H}_4\text{N}\cdot\text{SO}_3\text{H}$, m.p. 365—370°, converted by PCl_5 at 100° and then 140°, into pyridine-3-sulphonyl chloride (I) (sulphonamide, m.p. 110—111°), which with NHEt_2 in C_6H_6 gives pyridine-3-sulphondiethylamide (II), m.p. 49—50° (hydrochloride, m.p. 133—134°). With MeI - MeOH in a sealed tube at 100° for 6 hr. (II) yields the methiodide, m.p. 186—188° (methochloride, m.p. 160—174°). (I) and $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{NH}_2$ in C_6H_6 give pyridine-3-sulphonyl- α -phenylisopropylamide, m.p. 117—117.5° (methiodide; methochloride), whilst nicotinic acid, through the chloride, yields similarly nicotinyl- β -(α -phenylpropyl)amine, m.p. 100—101° (methiodide, m.p. 162—164°; methochloride, m.p. 60—70°). Coramine methiodide and methochloride, m.p. 175—176°, are prepared. Comparative physiological activities of the compounds are recorded. A. T. P.

Pyridonemethides. O. MUMM and R. PETZOLD (Annalen, 1938, 536, 1—29).—The product of the action of NaOH on Et₂ 1:4:6-trimethyl-2-methylene-1:2-dihydropyridine-3:5-dicarboxylate (I), regarded previously (A., 1924, i, 83) as Et 3-acetyl-1:4:6-trimethylpyrid-2-one-5-carboxylate, is shown to be Et 2-hydroxy-1:4:6-trimethyl-2:3-cyclobutanono-1:2-dihydropyridine-5-carboxylate (II). Diacetyldihydrocollidine suspended in Et₂O is oxidised by HNO_3 to diacetylcollidine, b.p. 159°/10 mm. (picrate, m.p. 198°). This is transformed by



Me_2SO_4 into the non-cryst. diacetyl-1-methylcollidine methosulphate (corresponding perchlorate, m.p. 190°), converted by 40% NaOH and CHCl_3 into diacetyl-trimethylpyridonemethide, which with 5*N*- NaOH at 90—100° gives NH_2Me and 4:6-diacetyl-3:5-di-

methylphenol, m.p. 109—110°, thus apparently supporting the older method of formulating (II). The prep. of (II) (corresponding *Me* ester, m.p. 115°) is amended. It is hydrolysed by dil. NaOH to 2-hydroxy-1:4:6-trimethyl-2:3-cyclobutanonodihydropyridine-5-carboxylic acid, m.p. 227° (*Ag* salt), which passes when evaporated with conc. HCl or heated at 240° into 2-hydroxy-1:4:6-trimethyl-2:3-cyclobutanonodihydropyridine, which does not fluoresce. Treatment of any derivative of (II) (except the phenylhydrazinoderivative) with conc. HCl at 120° under pressure leads to the fluorescent 1:4:6-trimethyl-1:2-dihydropyrid-2-one, m.p. 85° (hydrochloride, m.p. 208°; picrate, m.p. 155°). (I) is transformed by boiling H_2O into 5-carbethoxy-1:2:4:6-tetramethylpyridine-3-carboxybetaine, m.p. 240—241°. Et₂ collidinedicarboxylate dimethosulphate and conc. HCl at 120° give 1:2:4:6-tetramethylpyridine-3:5-dicarboxybetaine, m.p. 285°, Et₂ 4-benzyl-1:6-dimethyl-2-methylene-1:2-dihydropyridine-3:5-dicarboxylate affords 5-carbethoxy-4-benzyl-1:2:6-trimethylpyridine-3-carboxybetaine, m.p. 222°, whereas a betaine is not obtained from Et₂ 4-phenyl-1:6-dimethyl-2-methylene-1:2-dihydropyridine-3:5-dicarboxylate. $\text{NIHPh}\cdot\text{NH}_2$ and (II) in 50% AcOH give



Et 1:4:6-trimethyl-3- α -phenylhydrazinovinylpyrid-2-one-5-carboxylate (IV), m.p. 192°. 1:4:6-Trimethyl-3- α -phenylhydrazinovinylpyrid-2-one has m.p. 227°. Conc. HCl and (IV) at 120—130° give 3-2'-indolyl-1:4:6-trimethylpyrid-2-one, m.p. 141° (picrate, m.p. 163—164°). MgMeI and (II) give 1:4:6-trimethyl-3-isopropenylpyrid-2-one-5-carboxylic acid, m.p. 216° (decomp.). PCl_5 and (II) in CHCl_3 yield Et 1:4:6-trimethyl-3- α -chlorovinylpyrid-2-one-5-carboxylate (V), m.p. 84°. The corresponding *Me* ester, m.p. 89°, 1:4:6-trimethyl-3- α -chlorovinylpyrid-2-one, m.p. 114°, and Et 4-phenyl-1:6-dimethyl-3- α -chlorovinylpyrid-2-one-5-carboxylate (VI), m.p. 129—130°, are obtained analogously. Boiling 2*N*- NaOH converts (V) into 1:4:6-trimethyl-3- α -hydroxyvinylpyrid-2-one-5-carboxylic acid (VII), m.p. 185° (decomp.), whereas under these conditions (VI) yields Et 4-phenyl-1:6-dimethyl-3-acetylenylpyrid-2-one-5-carboxylate, m.p. 129°. At 70°/vac. (VII) loses H_2O with formation of 1:4:6-trimethyl-3-acetylenylpyrid-2-one-5-carboxylic acid (VIII), m.p. 185°. (VII) and CH_2N_2 give *Me* 1:4:6-trimethyl-3-acetylenylpyrid-2-one-5-carboxylate, m.p. 119°. The *Ag* salt of (VIII) and EtBr in boiling EtOH yield the corresponding Et ester, m.p. 66°. 1:4:6-Trimethyl-3- α -chlorovinylpyrid-2-one-5-carboxylic acid has m.p. 210° (decomp.). Examples of the re-conversion of substances with open chain into cyclobutane derivatives are cited. Hydrogenation (PtO_2 in AcOH) of (II) yields Et 2-hydroxy-2:3-hydroxycyclobutano-1:4:6-trimethylpyridine-5-carboxylate, m.p. (crude) 55—56°. Similarly obtained are Et 1:4:6-trimethyl-3-ethylpyrid-2-one-5-carboxylate, b.p. 203°/12 mm., m.p. 45°, 1:4:6-trimethyl-3-ethylpyrid-2-one, m.p. 78°, and

1:4:6-trimethyl-3-ethylpyrid-2-one-5-carboxylic acid, m.p. 211° (decomp.). H. W.

Absorption spectra of 4-(*p*-dimethylaminostyryl)pyridine methiodide and 2:4-di-(*p*-dimethylaminostyryl)pyridine methiodide. G. R. CLEMO and G. A. SWAN (J.C.S., 1938, 1454—1455).—*p*-NMe₂·C₆H₄·CHO with 4-methyl- and 2:4-dimethyl-pyridine gives respectively 4-, m.p. 255°, and 2:4-bis-(*p*-dimethylaminostyryl)pyridine methiodide, m.p. 318°. The absorption spectra of these compounds and of 2-(*p*-dimethylaminostyryl)pyridine methiodide show a strongly absorbing band at the blue end of the visible range. F. R. S.

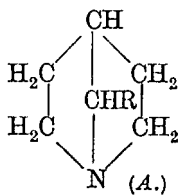
Reactions of Grignard reagents with isatin and *N*-alkylisatins. F. J. MYERS and H. G. LINDWALL (J. Amer. Chem. Soc., 1938, 60, 2153—2155).—Contrary to Kohn *et al.* (A., 1913, i, 757), *N*-methylisatin and MgPhBr (5 mols.) give 2:3-epoxy-2:3-diphenyl-1-methyldihydroindole, m.p. 137·5—138·5°, fluorescent, and 3:3-diphenyl-1-methyloxindole, m.p. 171—171·5°, non-fluorescent. The latter product is probably obtained from the former by dil. H₂SO₄ and is synthesised from 3:3-dichloro-1-methyloxindole, C₈H₆, and AlCl₃ at 50°. *N*-Ethylisatin and MgPhBr give similarly 2:3-epoxy-2:3-diphenyl-1-ethyldihydroindole, m.p. 116—117°, and 3:3-diphenyl-1-ethyloxindole, m.p. 156—157°, also obtained from 3:3-dichloro-1-ethyloxindole, C₈H₆, and AlCl₃. R. S. C.

Indole series. II. Derivatives of 2-phenylindole. E. B. WOMACK, N. CAMPBELL, and G. B. DODDS (J.C.S., 1938, 1402—1405).—HNO₂ with 3-oximino-2-phenylindole gives the 3-NO₂-compound, which with HNO₂ yields the 3:5-(NO₂)₂-derivative, also obtained by the method of Angeli *et al.* (A., 1901, i, 45). Oxidation (KMnO₄) of the 3-oximino- and 3-NO₂-compounds affords benzoylanthranilic acid, whilst the 3:5-(NO₂)₂-derivative gives 5-nitro-*N*-benzoylanthranilic acid, m.p. 257—260°, also prepared by benzylation of 5-nitroanthranilic acid to 5-nitro-*N*-benzoylanthranil, m.p. 178—180°, and subsequent hydrolysis. A trinitro-2-phenylindole could not be prepared. In properties, 3-nitroso-2-phenyl-1-methylindole resembles *p*-NO₂·C₆H₄·NMe₂. Nitration of deoxybenzoin gives the 2'-(2:4-dinitrophenylhydrazones, m.p. 219—221°) and 4'-NO₂-compounds (2:4-dinitrophenylhydrazones, m.p. 233—234°). Reduction of these compounds affords 2'-aminodeoxybenzoin, m.p. 170°, and the 4'-derivative respectively. An improved method for the prep. of *p*-nitrobenzil is given. F. R. S.

Formation of a quinolone derivative from *o*-aminoacetophenone and benzaldehyde. C. MANNICH and M. DANNEHL (Ber., 1938, 71, [B], 1899—1901).—*o*-C₆H₄Ac·NH₂ and 35% CH₂O in EtOH-H₂O give methylenedi-*o*-aminoacetophenone, CH₂(NH·C₆H₄Ac)₂, m.p. 144°, re-converted into its components by SO₂ and transformed by PhCHO and NaOH in EtOH into the dibenzylidene derivative, C₃₁H₂₄O₂N₂, m.p. 142°. PhCHO and *o*-C₆H₄Ac·NH₂ yield *o*-aminophenyl styryl ketone (I), m.p. 71°, which can be diazotised and coupled with β-C₁₀H₇·OH to a red dye. It gives a Bz compound, m.p. 119°, and is readily hydrogenated (Pd-C in EtOH) to *o*-amino-

phenyl β-phenylethyl ketone, m.p. 76° (semicarbazone, m.p. 196°). (I) can be distilled unchanged in a vac. but with NaOEt it passes into 4-keto-2-phenyl-1:2:3:4-tetrahydroquinoline, m.p. 149°, which cannot be diazotised. It gives a nitrosoamine, m.p. 121°, and Ac₂ derivative, m.p. 122°. H. W.

Substituted dicyclo[1:2:2]aza-1-heptane. V. PRELOG, E. CERKOVNIKOV, and (MLLE.) S. HEIMBACH (Coll. Czech. Chem. Comm., 1938, 10, 399—410; cf. A., 1937, II, 201; 1938, II, 466).—Tetrahydropyran-4-carboxylic acid (I) forms a chloride which with Zn-Me(Et)I-EtOAc gives tetrahydropyranyl Me, b.p. 90—94°/15 mm. (2:4-dinitrophenylhydrazones, m.p. 160—160·5°), and Et, b.p. 103°/15 mm. (2:4-dinitrophenylhydrazones, m.p. 146—146·5°), ketone, converted by Na in aq. Na₂CO₃-Et₂O into the corresponding methyl- (II), b.p. 112—114°/17 mm., and ethyl- (III), b.p. 115—118°/13 mm., carbinols. Tetrahydropyranylphenylcarbinol (IV), b.p. 112—113°/0·08 mm., is obtained from tetrahydropyran-4-aldehyde and MgPhBr. (II) and (III) and fuming HBr in a sealed tube at 100° for 3 hr. form αδ-dibromo-γ-bromoethyl-pentane (V), b.p. 120°/0·15 mm., and hexane (VI), b.p. 110—115°/0·06 mm., and α-bromo-γ-bromoethyl-Δ²-pentene, and hexene, b.p. 128—132°/16 mm., respectively, whereas (IV) yields only α-bromo-δ-phenyl-γ-bromoethyl-Δ²-butene, b.p. 160°/0·17 mm. The Me ester of (I) and RMgI yield 4-tetrahydropyranyl-dimethyl- (VII) (b.p. 118—123°/23 mm., diethyl-, m.p. 37—38°, diphenyl- (VIII), m.p. 172—173°, and dibenzylcarbinol, m.p. 177—177·5°, and, on drying the respective Et₂O extracts with Na₂SO₄, 4-isopropylidene- (IX), b.p. 54°/12 mm., and diethylmethylene-tetrahydropyran, b.p. 100—104°, also. (IX) is prepared also from (VII) by distilling with a little 2-C₁₀H₇·SO₃H and a trace of I. (VIII) and HCl-Et₂O at 0° form 4-benzhydrylidene-tetrahydropyran, m.p. 120°, but (VII) yields similarly 4-chloroisopropyltetrahydropyran, b.p. 83—85°/13 mm. The above pyranylcarbinols and 70% HBr at 100° yield α-dibromo-γ-isopropylidene-, b.p. 128—129°/9 mm., diethylmethylene-, b.p. 153—155°/12 mm., and benzhydrylidene-pentane, m.p. 73°. α-Bromo-δ-methyl-γ-bromoethyl-Δ²-pentene and Br-CCl₄ yield αγδ-tribromo-δ-methyl-γ-bromoethylpentane, m.p. 89—90°. (IX) and H₂ (Adams) yields 4-isopropyltetrahydropyran, b.p. 156—158°, 67—69°/17 mm., stable to KMnO₄ and aq. Br. (V) and (VI) and 20% NH₃-MeOH at 130—140° for 2½ hr. form 7-methyl- (A, R = Me) (platinichloride, m.p. 227·5°; picrate, m.p. 292°) and 7-ethyl- (platinichloride, m.p. 215·5°; picrate, m.p. 268—269°) dicyclo[1:2:2]aza-1-heptanes. A. T. P.



Norlupinane-octahydropyridocoline relationship. III. G. R. CLEMO, J. G. COOK, and R. RAPER (J.C.S., 1938, 1318—1319).—Me quinoline-2-carboxylate is reduced (H₂-PtO₂) to a mixture of Me deca-, b.p. 110—115°/1 mm. (picrolonate, m.p. 221—222°), and tetra-hydroquinoline-2-carboxylate, b.p. 135°/1 mm. (picrolonate, m.p. 172°). The H₁₀-ester and γ-bromobutyronitrile give Me 1-(γ-cyanopropyl)decahydroquinoline-2-carboxylate, b.p. 170—180°/1 mm., hydro-

lysed to *Me* decahydroquinoline-2-carboxylate-1- γ -butyrate, b.p. 160—170°/1 mm., which is cyclised (K) to 1-ketododecahydro-5:6-benzopyridocoline, b.p. 130°/1 mm. (picrolonate, m.p. 216°). Reduction of the ketone by the Clemmensen method affords 5:6-benzododecahydro-5:6-benzopyridocoline "B," b.p. 100—110°/1 mm. (picrate, m.p. 128—130°), and by the Wolff method yields the base "A," b.p. 100—110°/1 mm. (picrate, m.p. 148°). A similar series of reactions with the H_4 -ester leads to: *Me* 1-(γ -cyanopropyl)tetrahydroquinoline-2-carboxylate, b.p. 190—205°/1 mm.; *Me* tetrahydroquinoline-2-carboxylate-1- γ -butyrate, b.p. 180—185°/1 mm.; 1-keto-5:6-benzo-1:2:3:4:7:8-hexahydro-5:6-benzopyridocoline, b.p. 160°/1 mm.; and 5:6-benzo-1:2:3:4:7:8-hexahydro-5:6-benzopyridocoline "A," b.p. 120°/1 mm. (picrate, m.p. 174°), and "B," b.p. 120°/1 mm. (picrate, m.p. 142°, and picrolonate, m.p. 175°).
F. R. S.

2-Alkyl-1:2:3:4-tetrahydroisoquinoline hydrochlorides. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1938, 60, 2101—2103).—By the method of Wedekind *et al.* (A., 1902, i, 118) are prepared 2-methyl-, m.p. 227°, -ethyl-, m.p. 213°, -n-, m.p. 242°, and -iso-propyl-, m.p. 215°, -n-, m.p. 190°, and -iso-butyl-, m.p. 205°, -n-, m.p. 191°, and -iso-amyl-1:2:3:4-tetrahydroisoquinoline hydrochloride, m.p. 229°. *N*-Alkylation of homoveratrylamine by Decker's method succeeds only for the *Me* and *Et* compounds, and *EtI* with 6:7-dimethoxy-1:2:3:4-tetrahydroquinoline gives little of the 2-*Et* compound, but much quaternary salt. However, cyclisation of formhomoveratrylamine (prep. from the formate at 210°) by $POCl_3$ gives readily 6:7-dimethoxy-3:4-dihydroisoquinoline, the methiodide, ethiodide, m.p. 186.5°, *n*-, m.p. 158°, and iso-propiodide, m.p. 201° (decomp.), *n*-butiodide, m.p. 152°, *n*-, m.p. 123°, and iso-amylodide, m.p. 134.5°, of which are reduced by *Zn* powder in dil. H_2SO_4 at 100° to yield 6:7-dimethoxy-2-methyl-, -2-ethyl-, m.p. 246°, -2-*n*-, m.p. 223°, and -iso-propyl-, m.p. 268° (decomp.), -*n*-butyl-, m.p. 224°, -*n*-, m.p. 232°, and -iso-amyl-1:2:3:4-tetrahydroisoquinoline hydrochloride, m.p. 254°. With *HCl* at 165° these salts give 6:7-dihydroxy-2-ethyl-, m.p. 223°, -*n*-, m.p. 240°, and iso-propyl-, m.p. 253°, -*n*-butyl-, m.p. 202°, -*n*-, m.p. 187.5°, and -iso-amyl-1:2:3:4-tetrahydroisoquinoline hydrochloride, m.p. 208°. isoQuinoline *n*-amylodide has m.p. 139°. The salts have slight depressor effect and are strong sympatholytics. M.p. are corr.
R. S. C.

Syntheses in the 2-phenylquinoline series.
IV. Further reactions of azitrin with Grignard reagents. K. FEIST, W. AWE, and M. KUKLINSKI [with W. VÖLKSEN and H. EICHENTOPF] (Arch. Pharm., 1938, 276, 420—431; cf. A., 1938, II, 293).—*Et* 2-phenylquinoline-4-carboxylate and *MgPhBr* give a yellow substance (I), $C_{38}H_{25-26}ON_2$, m.p. 202—203° (dipicrate, m.p. 190°; diperchlorate, m.p. >300°), and small amounts of diphenyl-2-phenyl-4-quinolylcarbinol (II), m.p. 208°, and a substance, m.p. 196°, possibly a pinacone. 4-Cyano-2-phenylquinoline and *MgPhBr* give 2-phenyl-4-iminobenzylquinoline, m.p. 134°, hydrolysed to 4-benzoyl-2-phenylquinoline (III), m.p. 116° (picrate, m.p. 213.5°; oxime, m.p. 194°),

which with *MgPhBr* gives (II). (I) absorbs 2 H_2 catalytically, shows rather weakly the pharmacological action of atophan, and differs markedly from atophan, (II), and (III) (which resemble each other) in absorption spectrum. Its structure is discussed at length, but inconclusively.
R. S. C.

Preparation of 2:8-diaminoacridine. A. ALBERT and D. K. LARGE (Nature, 1938, 142, 435).—An investigation of the reaction between glycerol, $ZnCl_2$, $m-C_6H_4(NH_2)_2$, and $H_2C_2O_4$ yielding 2:8-diaminoacridine shows that (i) many substituted *m*-diamines are suitable for making substituted aminoacridines, (ii) *m*-substituted anilines are most reactive when the substituent, in descending order of activity, is NH_2 , NMe_2 , OH , and least active when it is *Me*, *Cl*, NO_2 , SO_3H , or CO_2H (NH_2Ph itself does not react), and (iii) in the case of $m-C_6H_4(NH_2)_2$ the final intermediate is probably 3:3'-diamino-*N*-formyldiphenylamine.
L. S. T.

Acridine compounds related to the 5-aminoacridine therapeutics. O. EISLEB (Med. u. Chem., 1936, 3, 41—59; Chem. Zentr., 1937, i, 604).—Acridines generally only active towards streptococci were prepared by Bernthsen's and by Ullmann's methods. 5-Aminoacridine and CH_2O yielded via an additive product, m.p. 110—118°, 5- β -hydroxyethylacridine, m.p. 154° (hydrochloride, decomp. 210—235°), from which were prepared 5- β -acetoxylethyl-, m.p. 120°, 5- β -bromethyl-, m.p. 200° (softening at 130—140°), 5-(β -ethanolmethylamino)ethyl- (dihydrochloride), and 5- β -piperidinoethylacridine, m.p. 137.5° (cf. A., 1934, 83) (diglycolate). Acridine-5-aldehyde afforded acridine-5-aldehydemethylimine, m.p. 160°, -5-aldehyde-ethanolimine, 5-(ω -nitro- α -hydroxyethyl)-acridine, decomp. 170°, 5-hydroxyethyl-, m.p. 178—180° (hydrochloride), 5- α -hydroxypropyl-, m.p. 158—159°, 5- α -hydroxybutylacridine, m.p. 121°, acridyl-5-p-ethoxyphenylcarbinol, m.p. 202°, 5- α -bromoethylacridine hydrobromide, 5- α -ethanolmethylaminoethylacridine (dihydrochloride), acridyl 5-*Me* ketone, m.p. 109°, oximinoacridyl 5-*Me* ketone, decomp. 195—200°, acridyl 5- CH_2Br ketone hydrobromide. The following derivatives of acridine-5-carboxylic acid were prepared: *Me* ester, m.p. 127—128°, β -diethylaminoethyl ester (hydrochloride, m.p. 190—191°), hydrazide, m.p. 236—244°, azide. 3-Ethoxy-5-methylacridine (from 2-bromo-4-ethoxyacetophenone and NH_2Ph followed by cyclisation or 2-chloroacetophenone and *m*-phenetidine followed by methylation), *Et* acridyl-5-acetoacetate, m.p. 130°, 5-acetonylacridine, m.p. 146°, 5-cyanoacridine, m.p. 183°, and -acridan are also described. The antistreptococcal action is more marked when a second NH_2 is introduced into the nucleus.
A. H. C.

5:5-Dialkylhydantoins containing a dialkylamino-substituent. J. W. MAGEE with H. R. HENZE (J. Amer. Chem. Soc., 1938, 60, 2148—2151).—5-Methyl-5-dialkylaminomethylhydantoins are prepared. $CH_2Br \cdot COMe$ and the appropriate *sec.* amine [1 mol. in aq. Na_2CO_3 (2 mols.) or 2 mols. in Et_2O] give di-methyl-, b.p. 31.6°/27 mm. (137°), -ethyl-, b.p. 69.6°/32 mm. (143°), -*n*-, b.p. 64.6°/8 mm. [150° (lit. 110°)], and -iso-propyl-, b.p. 79.7°/17 mm. (195°), -*n*-, b.p. 86.7°/3 mm. (132°), -iso-, b.p. 80.7°/9 mm.

[175° (lit. 132°)], and -*sec.-butyl-*, b.p. 104.7°/14 mm. (196°), -*iso-*, b.p. 78.7°/2 mm. [124° (lit. 166°)], and -*n-amyl-*, b.p. 110.2°/7 mm. (102°), and -*allyl-aminoacetone*, b.p. 80.7°/22 mm. (105°), figures in parentheses being the m.p. of the *semicarbazones*. With $\text{KCN}(\text{NH}_4)_2\text{CO}_3$ in hot 50% EtOH these products yield 5-methyl-5-di-methyl-, m.p. 177°, -ethyl-, m.p. 196°, -n-, m.p. 161°, and -iso-propyl-, m.p. 198°, -n-, m.p. 173°, -iso-, m.p. 222°, and -*sec.-butyl-*, m.p. 233°, -iso-, m.p. 204°, and -*n-amyl-*, m.p. 171°, and -*allyl-amino-methylhydantoin*, m.p. 135°. *d*, *n*, γ , and parachors are given for the NR_2 -ketones. Temp. are corr.

R. S. C.

Substituted barbituric acids.—See B., 1938, 1231.

Preparation and hypnotic action of triphenylmethylbarbituric acids. C. BERGGÄRDH (Acta Acad. Aboensis, 1936, 9, No. 3; Chem. Zentr., 1937, i, 357).—Barbituric acid (I) and CPh_3Cl yield *triphenylmethylbarbituric acid*, m.p. 274—275°, and thence with alkyl halide in alkaline solution, *triphenylmethyl-ethyl-*, m.p. 292—293°, and -*allyl-barbituric acid*, m.p. 310—311°. Hydrolysis to $\text{CPh}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, *triphenylmethyl-ethyl-*, m.p. 135—136°, and -*allyl-*, m.p. 147—148°, -*malonic acid* is described. Synthetic attempts from $\text{CPh}_3\cdot\text{CNa}(\text{CO}_2\text{Et})_2$ and $\text{CO}(\text{NH}_2)_2$ or guanidine or from the Mg compound of (I) and CPh_3Cl were fruitless. A. H. C.

Colour and chemical constitution. Organic and inorganic salts of diphenylvioluric acid. S. PRAKASH and S. DUTT (Proc. Nat. Acad. Sci. India, 1938, 8, 29—39).—Diphenylbarbituric acid with NaNO_2 and H_2SO_4 yields *diphenylvioluric acid*, m.p. 228° (decomp.) (Na , K , NH_4 , Li , NH_4Me , NHMe_2 , NMe_3 , NH_2Et , NHEt_2 , $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, $\text{NH}_2\text{Bu}^\beta$, $\text{NH}_2\cdot\text{CH}_2\text{Bu}^\beta$, NH_2Ph , *o-*, *m-*, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, $\text{C}_6\text{H}_5\text{Me}\cdot\text{NH}_2$, *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, *o*- and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, $\text{C}_5\text{H}_{11}\text{N}$, 2- $\text{C}_6\text{H}_4\text{NMe}_2$, 2:4:6- $\text{C}_6\text{H}_2\text{NMe}_3$, quinoline, isoquinoline, quinaldine, nicotine, morphine, brucine, cinchonidine, narcotine, quinine, quinidine, and codeine salts). *Di-p-tolyl-barbituric acid*, m.p. 157°, and -*violuric acid*, decomp. about 160° (NH_4 , NH_2Me , NMe_3 , NH_2Et , NHEt_2 , $\text{C}_5\text{H}_5\text{N}$, and $\alpha\text{-C}_5\text{H}_4\text{NMe}$ salts), *di-m-tolyl-barbituric acid*, m.p. 247°, and -*violuric acid*, m.p. 184° (decomp.) (NH_4 , NH_2Me , NH_2Et , $\text{C}_5\text{H}_5\text{N}$, and $\alpha\text{-C}_5\text{H}_4\text{NMe}$ salts), were prepared similarly. The colour of the acids and salts, and the change in colour in solution and adsorption max., and in certain cases hydrolysis const. and rotation, are recorded. The acids are pale yellow, whilst the salts are violet, corresponding with an oximino-ketonic and nitroso-enolic structure respectively. Substitution of the Ph leads to an increase in the adsorption max. F. R. G.

Spontaneous resolution of racemic histidine monohydrochloride. R. DUSCHINSKY (Festschr. E. C. Barell, Basel, 1936, 375—393; Chem. Zentr., 1937, i, 350; cf. A., 1934, 196).—The solubility isotherm of active and inactive histidine monohydrochloride shows that the latter is at 20—40° a true racemate with a transition point at 40—50°; the easy formation of supersaturated solutions allows the isolation of active forms and, by racemising remaining

material, the racemate may be converted completely into the biologically important *l*-form. A. H. C.

β -L-Aspartyl-L-histidine as a possible biological precursor of L-carnosine. V. DU VIGNEAUD and M. HUNT (J. Biol. Chem., 1938, 125, 269—274).—The chloride of $\alpha\text{-CH}_2\text{Ph}$ carbobenzyloxyaspartate and histidine Me ester in CHCl_3 give the *Ba* salt of carbobenzyloxy- β -L-aspartyl-L-histidine, hydrogenated (Pd-black) in dil. H_2SO_4 to β -L-aspartyl-L-histidine, m.p. 235—240° (decomp.), $[\alpha]_D^{25} +38^\circ$ in H_2O , which can replace histidine in rats' diet and thus may be a precursor of carnosine in nature; it has, however, no depressor activity. R. S. C.

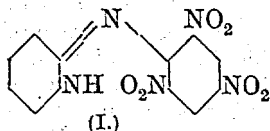
Behaviour of quaternary salts of cyclic bases towards sodium hyposulphite. P. KÄRRER, T. ISHII, F. W. KÄHNT, and J. VAN BERGEN (Helv. Chim. Acta, 1938, 21, 1174—1180; cf. A., 1938, II, 201).—2-Aminopyridine methiodide, m.p. 148—149°, is not reduced by $\text{Na}_2\text{S}_2\text{O}_4$. $\text{C}_5\text{H}_5\text{N}$ and $\text{C}_2\text{H}_4\text{Br}_2$ in EtOH at 100° give 1:1'-ethylenedipyridinium bromide, m.p. 295°, which is reduced to the bisdihdropyridine stage but yields a product which is too unstable to be isolated. Nicotinamide and $\text{C}_2\text{H}_4\text{Br}_2$ at 100° yield 1:1'-ethylenedinicotinamide bromide, incipient decomp. 282°, which affords 1:1'-ethylenebisdihydronicotinamide, marked decomp. 200° after becoming discoloured and incipient decomp. 175°, the composition of which is established by its absorption of nearly 4 H_2 when reduced catalytically (Pt) and of 2 O_2 when exposed to air in the presence of a trace of lactoflavin. Pyrimidine methiodide remains unchanged. 2:5-Dimethylpyrazine monomethiodide and moniodocetylolate, m.p. 128° after becoming brown at 100°, give H_2 -derivatives. H. W.

Quinoxalines.—See B., 1938, 1138.

Pyrido(1':2':1:2)benziminazoles and allied compounds (cyclic 1:3-diazalines). (SIR) G. T. MORGAN and (MISS) J. STEWART (J.C.S., 1938, 1292—1305).—Reduction ($\text{PtO}_2\text{-H}_2$) of the corresponding NO_2 -compound gives 5-amino-2:2'-dipyridylamine, m.p. 91°, which with 1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ forms 5-2':4'-dinitroanilino-2:2'-dipyridylamine, m.p. 198°, reduced catalytically to the -diamino-derivative, m.p. 187°. 2-Aminopyridine similarly affords 2-2':4'-dinitro-, m.p. 156—157°, and -diamino-anilinopyridine, m.p. 150°. The parent bases with picryl chloride yield 5-2':4':4''-trinitroanilino-2:2'-dipyridylamine, m.p. 224°, and 2-2':4':6'-trinitroanilinopyridine (I), m.p. 135° (with MeI forms the 2N-Me derivative, m.p. 243°). When heated (I) loses HNO_2 , giving 4:6-dinitropyrido(1':2':1:2)-benziminazole [7:9-dinitro-1:2-pyrido-4:5-benz-1:3-diazaline] (II), m.p. >300°, reduced ($\text{PtO}_2\text{-H}_2$) to the -diamino-compound, m.p. 204—205°, or partly reduced (Na_2S) to the 4:6- (or 6:4-) nitroamino-derivative, m.p. >280°. This compound is deaminated by diazotisation and treatment with EtOH- H_2O to 4- (or 6-)nitropyrido(1':2':1:2)-benziminazole, m.p. 260—262°, reduced catalytically to the -amino-compound, m.p. 229—230°, which is deaminated to the parent diazaline, pyrido-(1':2':1:2)benziminazole, m.p. 178—179°, isomeric with α -carboline. Catalytic reduction of (II)

under pressure gives 4:6-diamino-3':4':5':6'-tetrahydropyrido(1':2':1:2)benziminazole, m.p. 201—202°, deaminated to 3':4':5':6'-tetrahydropyrido(1':2':1:2)benziminazole, m.p. 107°, and converted by diazotisation and treatment with NaN_3 into 4:6-bistriazo-3':4':5':6'-tetrahydropyridobenziminazole, m.p. 132°. 4:6-Bistriazopyrido(1':2':1:2)benziminazole, m.p. 167—170°, is similarly obtained.

A comparable series of reactions with 2-amino-3-methylpyridine leads to 2-2':4':6'-trinitroanilino-3-methylpyridine, m.p. 142—143°, 4:6-dinitro-, m.p. 256—260°, -diamino-, m.p. about 130°, 4:6-(or 6:4-)nitroamino-, m.p. 269—270°, 4-(or 6-)nitro-, m.p. 260—262°, and 4-(or 6-)amino-3'-methylpyrido(1':2':1:2)benziminazole, m.p. 185—187°, and 3'-methylpyrido(1':2':1:2)benziminazole. [3'-methyl-1:2-pyrido-4:5-benz-1:3-diazaline], m.p. 162°. The corresponding compounds in the quinoline series are 2-2':4':6'-trinitroanilinoquinoline, m.p. >280°, 4:6-dinitro-, m.p. >300°, -diamino-, m.p. 273—274°, 4:6-(or 6:4-)nitroamino-, m.p. >300°, 4-(or 6-)nitro-, m.p. 242—243°, and 4-(or 6-)amino-quinolo(1':2':1:2)benziminazole, m.p. 220—223°, and quinolo(1':2':1:2)benziminazole [1:2-quinolo-4:5-benz-1:3-diazaline], m.p. 102°. The isoquinoline series affords 1-2':4':6'-trinitroanilinoisoquinoline, m.p. 156°, 4:6-dinitro-, m.p. >280°, -diamino-, m.p. 249—250°, and isoquinolo(2':1':1:2)benziminazole [1:2(2':1')isoquinolo-4:5-benz-1:3-diazaline], m.p. 129°. 9-2':4':6'-Trinitroanilino-phenanthridine gives 4:6-dinitro-, m.p. 280°, and -diamino-, and phenanthrido(10':9':1:2)benziminazole [1:2(10':9')-phenanthrido-4:5-benz-1:3-diazaline], m.p. 153—154°. The diazelines result from the loss of HNO_2 from substances of type (I). F. R. S.



Heterocyclic compounds containing nitrogen.
XXXVI. Reactions and ring closures with 1:3-dichloro-4:6-dinitrobenzene. II. **Benzo-dipyrrole.** IV. P. RUGGLI and O. STRAUB (Helv. Chim. Acta, 1938, 21, 1084—1100; cf. A., 1936, 614). —Addition of 1:3:4:6- $\text{C}_6\text{H}_2\text{Cl}_2(\text{NO}_2)_2$ (I) in C_6H_6 to a suspension of $\text{CHNaBz}\cdot\text{CO}_2\text{Et}$ in warm C_6H_6 yields Et_2 4:6-dinitrophenylene-1:3-dibenzoylacetate (II), m.p. 133°, catalytically reduced (Ni in $\text{EtOH}-\text{EtOAc}-\text{H}_2\text{O}$) with elimination of H_2O to Et_2 2:6-diphenylbenzodipyrrole-3:5-dicarboxylate, m.p. 325° after becoming brown at 310°. Ketonic fission of (II) leads to 4:6-dinitro-1:3-diphenacylbenzene, m.p. 170—171°, hydrogenated to 2:6-diphenylbenzodipyrrole, m.p. >300°. One-sided condensation of (I) with $\text{CHNaBz}\cdot\text{CO}_2\text{Et}$ in abs. C_6H_6 yields a non-cryst. product, hydrolysed by conc. H_2SO_4 to 5-chloro-2:4-dinitrodeoxybenzoin, m.p. 130°, in 70% yield. $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ and (I) yield *Et* cyano-5-chloro-2:4-dinitrophenylacetate, m.p. 108—109° after softening, which with further quantities of $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ gives only initial material or resin. With deoxybenzoin (I) gives 1-chloro-4:6-dinitro-3-desylbenzene (III), m.p. 130—131° [(?)-phenylhydrazone, m.p. 195—196°]. CHNaAcBz and (I) yield benzoyl-5-chloro-2:4-dinitrophenylacetone, m.p. 130—131°, con-

verted by conc. HCl in boiling EtOH into (III), which with $\text{NHPh}\cdot\text{NH}_2$ in boiling EtOH (protracted heating) gives the phenylhydrazone of 6-nitro-5-phenacyl-2-phenyl- ψ -azimidobenzene, m.p. 197—198°. Condensation of (I) with indandione by NaOEt in C_6H_6 or, preferably, in EtOAc yields 2:5'-chloro-2':4'-dinitroindandione, m.p. 184—185° (decomp.). 2:5'-Chloro-2':4'-dinitrophenylbindone, decomp. 218°, is described. Et_2 dinitrophenylenediaceacetate and BzCl in $\text{C}_5\text{H}_5\text{N}$ afford the *O*- Bz_2 derivative, m.p. 166—167°. Benzoylation of 4:6:1:3-(NO_2) $_2\text{C}_6\text{H}_2(\text{CH}_2\text{Ac})_2$ (IV) in $\text{C}_5\text{H}_5\text{N}$ yields the *O*- Bz_2 derivative, m.p. 139—140°, characterised by its insolubility in alkali and ready hydrolysis by $\text{HCl}-\text{EtOH}$ to the initial material; a *C*- Bz derivative could not be prepared. PhNO and (IV) in hot EtOH containing $\text{KOH}-\text{MeOH}$ yield the dianil of 4:6-dinitrophenylene-1:3-di(methylglyoxal), m.p. 174—175° (decomp.), hydrolysed by 50% $\text{H}_2\text{SO}_4-\text{EtOH}$ to 4:6-dinitrophenylene-1:3-di(methylglyoxal), m.p. 118—119° (corresponding quinoxaline derivative, m.p. 238—239°). This is transformed by PhN_2Cl and anhyd. NaOAc in EtOH into the $\alpha\alpha'$ -diphenylhydrazone, decomp. 215°, which is unaffected by acids but transformed by alkalis into 3:5-diacetyl-1:7-diphenylbenzodipyrzole, m.p. 310—312°, whereas the corresponding $\beta\beta'$ -di(phenylhydrazone), decomp. 234° after darkening, obtained from the tetraketone and $\text{NHPh}\cdot\text{NH}_2$ in boiling EtOH , is converted by NaOH into 1:8-diphenyl-3:6-dimethylbenzodipyrzazolone, m.p. 353—354° (decomp.). Et_2 4:6-dinitrophenylene-1:3-diacetate either does not react with $\text{Et}_2\text{C}_2\text{O}_4$, or gives resinous products. When heated with *p*- $\text{NO}-\text{C}_6\text{H}_4\text{NMe}_2$ it does not condense but yields initial material and smeary masses also obtained by use of $\text{NaOH}-\text{EtOH}$. With PhNO in EtOH containing piperidine at 65° it condenses one-sidedly to Et_2 4:6-dinitrophenylene-3-acetate-1-glyoxylate, m.p. (indef.) 116—120° (phenylhydrazone, m.p. 154—155°). $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}, \text{HCl}$, (I), and cryst. NaOAc in boiling EtOH yield Et_2 4:6-dinitrophenylene-1:3-diaminoacetate, m.p. 197—198°, and *Et* 1-chloro-4:6-dinitrophenyl-3-aminoacetate, m.p. 145—146°, converted into the di-ester by treatment with $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}, \text{HCl}$ and NaOAc ; catalytic hydrogenation of it does not appear to give homogeneous products. (I), $(\text{CH}_2\cdot\text{OH})_2$, and NaOH give 4:6-dinitro-1:3-di- β -hydroxyethoxybenzene, m.p. 135—136° (Ac_2 , m.p. 90—91°, and Bz_2 , m.p. 164—165°, derivatives), catalytically reduced (Rupe Ni in $\text{EtOAc}, \text{EtOH}-\text{H}_2\text{O}$) and then acetylated (Ac_2O) to 4:6-diacetamido-1:3-di- β -hydroxyethoxybenzene, m.p. 205—207°. $(\text{NO}_2)_2\text{C}_6\text{H}_2(\text{NHPh})_2$ is converted by boiling Ac_2O and melted ZnCl_2 into its Ac_2 derivative, m.p. 232—233°. H. W.

Heterocyclic compounds containing nitrogen.
XXXV. 4:6-Dinitro- and -diamino-isophthalaldehyde. II. *lin.* **Benzo-di- α -picoline and benzo-dipyridine.** P. RUGGLI, P. HINDERMANN, and H. FREY (Helv. Chim. Acta, 1938, 21, 1066—1083; cf. A., 1937, II, 214). —4:6-Dinitroisophthalaldehyde (I) and $\text{C}_5\text{H}_5\text{N}$ react in a complex manner at 60—100°, evolving CO_2 and nitrous fumes and giving a compound, $\text{C}_{25}\text{H}_{18}\text{O}_6\text{N}_2$, m.p. >300°, which appears to contain a phenolic OH and a basic group. Homogeneous products have not been obtained by condens-

ing (I) with barbituric acid, indandione, or phenylmethylpyrazolone. The compound obtained from (I) and CH_2N_2 is mainly not dinitrodiacetylbenzene (*loc. cit.*) but the isomeric dinitrodioxidoethylenylbenzene, m.p. 153—154° (with small amounts of a compound, m.p. 93°), since it is converted by HCl in $\text{C}_5\text{H}_5\text{N}$ into 4:6-dinitro-1:3-di- β -chloro- α -hydroxyethylbenzene, m.p. 150—151°. Hydrolysis of Et_2 4:6-diaminophenylene-1:3-diacrylate with boiling conc. HCl gives 4:6-diaminophenylene-1:3-diacrylic acid hydrochloride (II), gradual decomp. $>280^\circ$ after softening at 270° (Ac_1 , decomp. $\sim 320^\circ$, and Ac_2 , decomp. $\sim 320^\circ$, derivatives of 4:6-diaminophenylene-1:3-diacrylic acid), and 7-aminocarbostyryl-6-acrylic acid, decomp. $>300^\circ$. With conc. HCl at 160° (II) affords 2:7-dihydroxybenzodipyridine, slow decomp. $>400^\circ$. Diaminoisophthalaldehyde (III) gives 4:6-diaminoisophthalaldibarbituric acid, m.p. $>300^\circ$ (Ac_1 derivative), and is converted by $\text{CH}_2(\text{CO}_2\text{Et})_2$ in boiling xylene containing a little piperidine into the compound, $\text{C}_{13}\text{H}_{14}\text{O}_5\text{N}_2$, m.p. 154—157° and, after re-solidification, m.p. 195—200° (decomp.). *p*-Methoxyacetophenone and (III) in presence of a little KOH-MeOH at 150° yield 2:7-di-*p*-anisylbenzodipyridine, m.p. 268—269° (*picrate*). CH_2Ac_2 , (III), and piperidine at 180 — 190° afford 3:6-diacetyl-2:7-dimethylbenzodipyridine dihydrate, m.p. 213—215° (corresponding *dipicrate* without characteristic m.p.), transformed by boiling Ac_2O into the compound, $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2\text{Ac}_2\text{O}$, which passes when warmed into 3:6-diacetyl-2:7-dimethylbenzodipyridine, m.p. 211—212° after softening at 191° (*dioxime*, m.p. 255—257°). With Et_2 oxalacetate in boiling xylene containing piperidine (III) gives Et_4 benzodipyridine-2:3:6:7-tetracarboxylate, m.p. 212° , and, mainly, an ill-defined, amorphous product, m.p. (indef.) $>300^\circ$, also obtained by use of $\text{C}_5\text{H}_5\text{N}$. One-sided condensation of $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ with (III) in presence of piperidine at 150° leads to 7-amino-3-benzoyl-6-aldehydocarbostyryl, m.p. 278—279° (decomp.) after softening at 260° , in 95% yield (*Ac* derivative, decomp. $\sim 320^\circ$). $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and (III) in EtOH containing 9—10% of NaOH at 30° afford Et_2 2:7-dimethylbenzodipyridine-3:6-dicarboxylate (IV), hydrolysed to 2:7-dimethylbenzodipyridine-3:6-dicarboxylic acid (+ H_2O); this is decarboxylated at 175 — $180^\circ/10$ — 13 mm. to 2:7-dimethylbenzodipyridine (benzodi- α -picoline) (V), m.p. 196—197°, also obtained with an isomeride (? polymeride) by direct hydrolysis of (IV) with conc. HCl at 130° . (V) gives a *dipicrate*, decomp. 220° after becoming discoloured at 160° , a *monoperchlorate*, decomp. 228 — 230° , a *diperchlorate*, explosive decomp. 318° , a *chromate*, explodes at 100° , a *monomethiodide*, slow decomp. $>244^\circ$, a *dibenzylidene*, m.p. 279° , and a *difurfurylidene*, decomp. 271.5 — 272.5° , derivative. Removal of Me from (V) could not be accomplished by the usual methods but bromination of (V) by Br in AcOH containing NaOAc at 70° leads to 2:7-di-(tribromomethyl)benzodipyridine, decomp. 190 — 192° , hydrolysed by 10—15% oleum to benzodipyridine-2:7-dicarboxylic acid. This is transformed by Cu powder, anhyd. $\text{Ba}(\text{OH})_2$, and BaO at 230 — $240^\circ/\text{vac.}$ into lin.-benzodipyridine [1:8-diaza-anthracene], m.p. 164.5 — 165° [*picrate*, m.p. 262° (decomp.) after softening at 239°].

H. W.

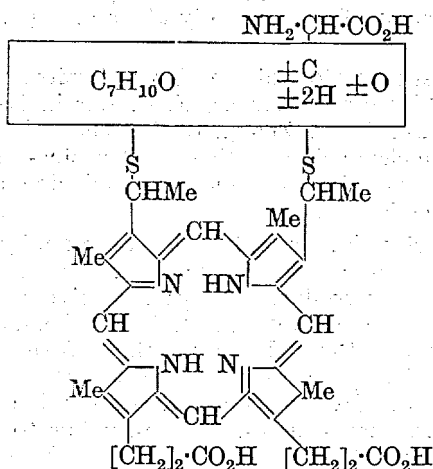
Synthesis of hetero-rings containing nitrogen. XIII. Synthesis of dibenzoquinolizine derivatives. Synthesis of 4':5':4'':5''-tetramethoxy-1:2:5:6-tetrahydro-[1':2':3:4-, 1'':2'':7:8-dibenzoquinolizine]. S. SUGASAWA and K. KAKEMI (Ber., 1938, 71, [B], 1860—1864).—An account of work already abstracted (A., 1938, II, 378). H. W.

Yeast-nucleic acid and its fission products. F. C. MEMMEN (Festschr. E. C. Barell, Basel, 1936, 520—527; Chem. Zentr., 1937, i, 363).—The prep. of yeast-nucleic acid and thence adenosine- and guanosine-phosphoric acids, guanosine, adenine, and hypoxanthine is reviewed. A. H. C.

Distribution coefficients of porphyrins between ether and hydrochloric acid. Applications to problems of quantitative separation. A. KEYS and J. BRUGSCH (J. Amer. Chem. Soc., 1938, 60, 2135—2139).—Determination of the concn. of porphyrins by fluorescence spectra of their solutions is described. HCl coeffs. are accurately determined for copro-, hamato-, meso-, deuterio-, and proto-porphyrin, and for phylloerythrin and are const. for 0.025—10% HCl and for 5×10^{-8} to 2×10^{-3} g. of porphyrin per l. Successive extractions give theoretical results until extraction is 85% complete. Extraction of mixed porphyrins gives correct results (within 5%) and is semiquant. for <0.01 mg. of substance. R. S. C.

Action of light on porphyrins. II. H. FISCHER and H. BOCK (Z. physiol. Chem., 1938, 255, 1—13; cf. A., 1938, II, 116).—When air is passed through a $\text{C}_5\text{H}_5\text{N}$ solution of the Me_2 ester (I) of protoporphyrin (II) exposed to sunlight trihydroxyprotoporphyrin Me_2 ester (III), m.p. 212° (*Cu* salt), is obtained. Exposure of a $\text{C}_5\text{H}_5\text{N}$ solution of (II) to electric light followed by treatment with CH_2N_2 yields dihydroxyprotoporphyrin Me_2 ester (IV), m.p. 221° . The spectra of (III) and (IV) are identical. (IV) is partly converted by Pd- H_2 into mesoporphyrin (V) when AcOH is the solvent but mainly into mesochlorin together with a little (V) when COMe_2 is the solvent. (I) in COMe_2 with Pd- H_2 yields (V) but no chlorin. When air is passed through a $\text{C}_5\text{H}_5\text{N}$ solution of aetioporphyrin-I (VI) exposed to electric light and the product is purified by adsorption on Al_2O_3 followed by elution with CHCl_3 -MeOH the substance, $\text{C}_{32}\text{H}_{38}\text{ON}_4$, m.p. 208° (decomp.) (*oxime*), the substance, $\text{C}_{32}\text{H}_{38}\text{O}_3\text{N}_4$, m.p. 259° , and the substance, $\text{C}_{32}\text{H}_{38}\text{O}_3\text{N}_4$, m.p. 203° (decomp.), are obtained. Similarly the Me_2 ester of pyrroporphyrin (VII) yields (with sunlight) dihydroxypyrroporphyrin Me_2 ester, $\text{C}_{32}\text{H}_{36}\text{O}_4\text{N}_4$, the Me_2 ester of (V) yields (with electric light) dihydroxymesoporphyrin Me_2 ester, $\text{C}_{36}\text{H}_{42}\text{O}_6\text{N}_4$, m.p. 189° , and phylloporphyrin Me_2 ester yields (with sunlight) the substance, $\text{C}_{32}\text{H}_{38}\text{O}_4\text{N}_4$, m.p. 218° , a substance, m.p. 242° (decomp.), and a substance, m.p. 263° . Rhodoporphyrin is only slightly affected by photo-oxidation. With ClSO_3H (V) gives mesorhodin, (VII) gives pyrro-rhodin, and (VI) gives tetrachloro-aetioporphyrin (*Cu* salt, m.p. 273° ; *Fe* salt, m.p. $>320^\circ$). The prep. of bromopyrro-aetioporphyrin (VIII), m.p. 320° (decomp.) (erroneously stated to be a peroxide in Part I), is described. (VIII) in boiling quinoline gives with CuCN the corresponding nitrile. W. McC.

Constitution of cytochrome C. H. THEORELL *Biochem. Z.*, 1938, **298**, 242—267; cf. A., 1937, III, 411).—Porphyrin *c*, $C_{45}H_{54}O_9N_6S_2$ (<5% ash), is a brown, slightly hygroscopic powder insol. in neutral solns. It contains 2 α -NH₂, 4 CO₂H, and 2 S resistant to alkali. It is formulated as:



Porphyrin *c* in AcOH-NaCl with Fe(OAc)₂ gives monoaminodithiochlorhæmin *c*, $C_{39}H_{43}O_6N_5S_2FeCl$, from which monoaminodithiohæmatin *c*, $C_{39}H_{43}O_6N_5S_2FeOH$, was prepared. Diaminodithiohæmatin *c*, $C_{45}H_{52}O_9N_6S_2FeOH$, was prepared from porphyrin *c* by the action of reduced Fe in AcOH.

C. C. N. V.

Phthalocyanines.—See B., 1938, 1138.

Properties of isosteric and structurally similar compounds. VII. Dissociation constants of 2:4-diketo-5:5-dialkyl-oxazolidines and -thiazolidines. H. ERLÉNMEYER, A. KLEIBER, and A. LOEBENSTEIN (*Helv. Chim. Acta.*, 1938, **21**, 1010—1013; cf. A., 1938, II, 382).—COMeEt, KCN, and KCNS are condensed by 30% HCl to 4-keto-2-thion-5-methyl-5-ethyl-oxazolidine, m.p. 106°, converted by Pb(OAc)₂ or, better, by Br-H₂O into 2:4-diketo-5-methyl-5-ethyl-oxazolidine, b.p. 147—148°/11 mm., m.p. 31°. Measurements of the dissociation const. of 2:4-diketo-5:5-dimethyl-, -5:5-diethyl-, -5:5-dipropyl-, and -5:5-diallyl-thiazolidine and of 2:4-diketo-5:5-dimethyl-, -5-methyl-5-ethyl-, and -5:5-diethyl-oxazolidine show that the oxazolidines are stronger acids than the corresponding thiazolidines. Within a series the acidity increases with increasing no. of C in the alkyl groups. The diallyl compound is more acidic than the corresponding Prⁿ₂ derivative.

H. W.

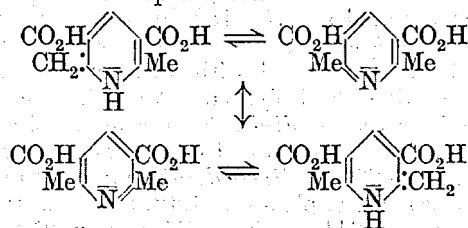
isoOxazole group. V. **isoOxazole aldehydes.** A. QUILICO and L. PANIZZI (*Gazzetta*, 1938, **68**, 411—421).—Ordinary methods of reducing CO₂H to CHO are inapplicable in the *isooxazole* group. 3-Phenyl-5-methylisooxazole-4-carboxylanilide (A., 1938, II, 33) with PCl₅ in PhMe gives the 4-*iminochloride*, m.p. 103—104.5°, which with SnCl₂-HCl in Et₂O (A., 1920, i, 58) gives CH₂BzAc (the first *isooxazole* ring fission under acid conditions), and, in poor yield, 3-phenyl-5-methylisooxazole-4-aldehyde (I), m.p. 55—56° [*phenylhydrazone*, m.p. 102—103.5°; *p*-nitrophenylhydrazone, m.p. 211—212°; *oxime*, m.p. 134—135°;

semicarbazone, m.p. 182—193.5° (?), stable in air and to NaOH, oxidised (KMnO₄-Na₂CO₃) to the acid (II). With Piloty's acid, (I) furnishes 3-phenyl-5-methyl-4-isooxazolylhydroxamic acid, m.p. 182—183° (decomp.), also obtained from (II) and NH₂OH. E. W. W.

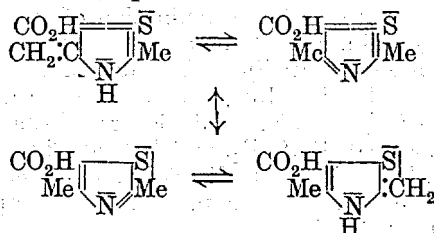
Syntheses from ethanolamine. V. **Synthesis of Δ^2 -oxazoline and of 2:2'- Δ^2 -dioxazoline.** H. WENKER (*J. Amer. Chem. Soc.*, 1938, **60**, 2152—2153; cf. A., 1937, II, 149).—SOCl₂ and CHO·NH·[CH₂]₂·OH (I) give impure *form*- β -chloroethylamide (II), b.p. 137—138° (decomp.)/20 mm. (with CO and Cl·[CH₂]₂·NH₂), which with 50% KOH at 15—18° gives Δ^2 -oxazoline, b.p. 98° (picrate, an oil), hydrolysed by H₂O to (I), by HCl-Et₂O to (II), decomposed by Na (gives NaCN and other products), and yielding an alkaline solution in H₂O. (CO·NH·[CH₂]₂·OH)₂ and SOCl₂ in PhMe give *s*-di- β -chloroethylloxamide (III), m.p. 203°, converted by hot *n*-KOH-MeOH into di-2- Δ^2 -dioxazolinyl, m.p. 213° (picrate, m.p. 182°), neutral in H₂O and hydrolysed by HCl-Et₂O to (III). R. S. C.

Dislite. R. FUSCO (*Gazzetta*, 1938, **68**, 380—386).—Dislite (I) (Baup, *Annalen*, 1852, **81**, 102; Bassett, *J.C.S.*, 1891, **59**, 978), $C_8H_6O_6N_4$, is now obtained from the mother-liquors of eulite prepared from citraconic acid and HNO₃ (A., 1936, 617, 1129). It is stable to HCl or H₂SO₄; with NaOEt-EtOH it gives a Na salt. With SnCl₂-HCl it gives a product, $C_8H_{10}O_2N_4$, m.p. 167° (*Ac*₂ derivative, m.p. 240°; *Bz*₂ derivative, m.p. 254°). Heated with PhCHO and NHEt₂ it gives a product, $C_8H_2O_6N_4$ (·CHPh)₂, m.p. 220—250°; similar products; $C_8H_2O_6N_4$ (·CH·C₆H₄·OMe)₂, m.p. 206—208°, and $C_8H_2O_6N_4$ (·CH·CH·CHPh)₂ are also obtained. Thus (I) contains 2 CH₂·NO₂, and is probably 3:3'-(or 5:5'- or 3:5'-)*di*(nitromethyl)-5:5'-(or 3:3'- or 5:3'-)*diisooxazolyl*. E. W. W.

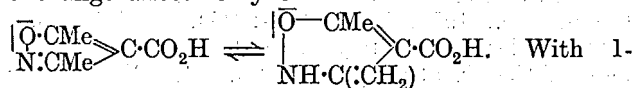
Structure of heterocyclic aromatic compounds with deuterium as indicator. II. H. ERLÉNMEYER, H. M. WEBER, and P. WIESSMER (*Helv. Chim. Acta*, 1938, **21**, 1017—1022; cf. A., 1938, II, 382).—2:6-Dimethylpyridine-3:5-dicarboxylic acid exchanges 8 H in D₂O. Mesomerism and tautomerism are represented:



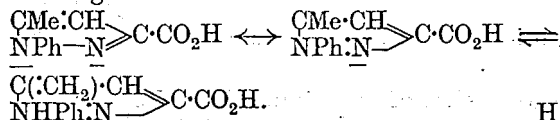
The similar result with 2:4-dimethylthiazole-5-carboxylic acid is represented:



With 3:5-dimethylisooxazole-4-carboxylic acid the exchange affects only one Me:



With 1-phenyl-5-methylpyrazole-3-carboxylic acid 4 H are exchanged:



H. W.

Aldehydes derived from heterocyclic rings.—See B., 1938, 1135.

Selenylbenzthiazoles and benzselenazoles.—See B., 1938, 1200.

Oxidations with hypiodite. II. Heterocyclic compounds containing nitrogen. Determination of aneurin (vitamin-B₁). K. H. SLOTTA and K. NEISSER (Ber., 1938, 71, [B], 1984—1986).—The acid or neutral solution containing 0.8—4 mg. of aneurin hydrochloride is treated with 10 c.c. of 0.01N-I and cooled in ice. Rather more 2N-NaOH is added than is required to decolorise the I and the mixture is kept at 0°, preferably in the dark, for 1.5—2 hr. It is then acidified and titrated at 0° with 0.05N-Na₂S₂O₃. Aneurin and I react in the const. mol. ratio, 1:6 (= 12 I). H. W.

Peganine (vasicine). E. SPÄTH (Monatsh., 1938, 72, 115—142).—A literature survey. A. T. P.

Action of resorcinol on the dihydrochlorides of quinine alkaloids. M. ROSSIGNOL and A. RIBOULLEAU (Compt. rend., 1938, 207, 495—497).—Equimol. amounts of quinine, quinidine, cinchonine, and cinchonidine dihydrochlorides with *m*-C₆H₄(OH)₂ in hot H₂O afford cryst. additive products. The following are described [R = *m*-C₆H₄(OH)₂]: *quinine*, R, 2HCl, H₂O (I); *quinidine*, R, 2HCl; *cinchonine*, R, 2HCl (II); and *cinchonidine*, R, 2HCl, H₂O (III). (II) and (III) turn pale brown gradually when exposed to light or air, or for a long period at 95—100°. (I) and (III) become opaque in a short time at 95—100°; the others are unchanged. J. L. D.

Ergot alkaloids. XIV. Positions of the ethylenic linking and the carboxyl group in lysergic acid and its isomeride. Structure of the alkaloids. L. C. CRAIG, T. SHEDLOVSKY, R. G. GOULD, jun., and W. A. JACOBS (J. Biol. Chem., 1938, 125, 289—298; cf. A., 1938, II, 117).—Comparison of the dissociation consts. of NH₂Et, the Et esters of alanine and β-alanine, 6-methylergoline, α- and γ-dihydrolysergic, lysergic (I), and isolysergic acid (II), ergometrine, ergometrinine, dihydroergometrine, dihydroergometrinine, α- and β-dihydrolysergol shows that (a) the CO₂H is in position 8 and (b) the ethylenic linking in ring c is in position 5—10 (or, less probably, 4—5) in (I) and the ergotoxine series of alkaloids, and in position 10—9 in (II) and the ergotinine series. R. S. C.

Alkaloids of *Alstonia* barks. III. Alstonine. T. M. SHARP (J.C.S., 1353—1357).—Alstonine (I) is reduced (H₂-PtO₂) to *tetrahydroalstonine* (II), m.p. 230—231°; [α]_D -107.0° in CHCl₃ [hydrochloride,

m.p. 298° (decomp.), [α]_D -15.75° in MeOH; *methiodide*, m.p. 236° (decomp.)], which is hydrolysed (KOH) to *tetrahydroalstoninic acid hydrochloride*, m.p. 296° (decomp.), [α]_D -22.1° in MeOH, re-esterified (MeOH) to (II). This indicates that (I) and (II) are Me esters. The sulphate of (I) with Br-H₂O gives a substance, converted by EtOH into a compound, C₂₁H₁₈O₄N₂Br₂·HBr, m.p. 276° (decomp.), which is reduced (H₂-PtO₂-CaCO₃) to a mixture of bases, isolated as the sulphate, C₂₁H₂₁O₄N₂Br·0.5H₂SO₄, m.p. 212° (decomp.), [α]_D -13.6° in H₂O, and the *hydrobromide*, C₂₁H₂₂O₃N₂·HBr, m.p. 291° (decomp.), [α]_D +162.8° in MeOH. Oxidation (KMnO₄) of the sulphate of (I) yields a mixture from which *N*-oxalylanthranilic acid is isolated. Se dehydrogenation of (I) affords Me₂Se₂ and *alstyrine*, C₁₈H₂₀N₂ or C₁₉H₂₂N₂, m.p. 113° [*picrate*, m.p. 215—216°; *methiodide*, m.p. 221° (decomp.)]. *Alstyrine* methochloride is reduced (H₂-PtO₂) to a methine base, which with MeI gives *alstyrine hydromethine methiodide*, C₁₈H₂₅N₂Me₂I, m.p. 227° (*methochloride*, m.p. 196—197°). Reduction (H₂-PtO₂) of *alstonine* methochloride affords *alstonine hydromethine base*, C₂₁H₂₃O₃N₂Me, m.p. 182—183°, methylated further to *alstonine hydromethine methiodide*, m.p. 276° (decomp.); the methochloride corresponding with the latter is catalytically reduced to a compound, C₂₂H₂₇O₃N₂I, m.p. 257°. F. R. S.

Curarine from calabash curare. II. H. WIELAND and H. J. PISTOR (Annalen, 1938, 536, 68—77; cf. A., 1937, II, 127).—The amounts of toxiferine (I) isolated as the anthraquinonesulphonate from samples of the arrow poison from various parts of Venezuela are the same as those reported previously (*loc. cit.*) so that the same plants are used by the natives of these regions. The bark and ground wood of *Strychnos toxifera* from British Guiana does not contain (I), its place being taken by an alkaloid with 6—8-fold greater curare action and much extended paralytic effect. The differences are not due to the rough methods of extracting (I). Calabash curare is therefore derived from different plants. The name "toxiferin" is therefore withdrawn in favour of *calabash curarine* I (II) or, shortly, *C-curarine*-I. The anthraquinonesulphonate (III) of (II) (*loc. cit.*) is converted into the *aurichloride*, m.p. 223—224° (decomp.), and thence into the *hydrochloride* (IV), C₂₀H₂₃ON₂Cl, m.p. >350° after becoming discoloured at 240°, [α]_D²⁰ +73.6° in H₂O, also obtained without intermediate formation of (III). The *hydriodide*, m.p. >320°, *perchlorate*, 2-naphthalenesulphonate, *platinichloride*, and *carbonate* have been obtained. Contrary to previous observation, (II) is a quaternary NH₄ base, formed by the action of Ag₂O on (IV) in the complete absence of CO₂. Evaporation of the cold solution causes loss of H₂O and formation of a tert. base, C₄₀H₄₂ON₄, m.p. 148° (decomp.) after softening at 130°. It is undecided whether this is an ether-like decomp. product or the base has the doubled mol. formula. *Calabash-curarine* II (V) is isolated as the *hydrochloride*, C₂₀H₂₅ON₂Cl, m.p. >320° after becoming brown at 220°, [α]_D²⁰ +74.3° in H₂O, as by-product of (II); physiologically it is much less active than the main

alkaloid. It is a strong quaternary NH_4 base which readily passes into a *tert.* base. The *hydriodide* and the unstable *aurichloride* are described. (V) is possibly the H_2 -derivative of (II). H. W.

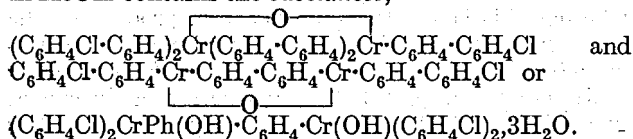
Sulphophenylarsinic acids and their derivatives. I. *p*-Sulphophenylarsinic acid. J. F. ONETO (J. Amer. Chem. Soc., 1938, 60, 2058—2059).—Contrary to Barber (A., 1930, 1456) *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ gives by the Bart reaction 28% of *Na p-sulphophenylarsinate*, converted by way of the *Ba* salt into the free acid, m.p. $>300^\circ$, which with HI or $\text{HBr}\cdot\text{SO}_2$ gives *Na di-iodo-* (I) and *Na dibromo-p-sulphophenylarsine* (II), *cryst.*, respectively. With piperidine *N*-pentamethylenedithiocarbamate in hot 50% EtOH (I) yields *piperidine p-sulphophenylarsylene bis-N-pentamethylenedithiocarbamate*, *decomp.* $230\text{--}232^\circ$. With hot, aq. NaOH (II) gives *Na p-sulphophenylarsine oxide*, *cryst.*, $+3\text{H}_2\text{O}$ and anhyd.

R. S. C.

Syntheses in the quinoline series. I. 2-Hydroxy- and 2-chloro-quinolinearsinic acids. J. D. CAPPS and C. S. HAMILTON (J. Amer. Chem. Soc., 1938, 60, 2104—2106).—Preps. of 5-, 6-, and 7-nitroquinoline, their 2-OH-derivatives, 5- and 7-amino-2-hydroxyquinoline, and 7-amino-2-hydroxy-4-methylquinoline [from *m*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ at 130°] are outlined. Hydrogenation of 2-chloro-5- and -8-nitroquinoline in COMe_2 at 50° gives 2-chloro-5-, m.p. $110\text{--}111^\circ$, and -8-aminoquinoline, m.p. 84° , respectively. 2-Chloro-6-aminoquinoline, m.p. 149° , is obtained by SnCl_2 -reduction of the NO_2 -compound. By the Bart reaction the amines yield 2-hydroxy-4-methylquinoline-7-arsinic acid, anhyd. and $+\text{H}_2\text{O}$ (*Na* salt, anhyd. and $+2\text{H}_2\text{O}$), 2-hydroxyquinoline-5-, anhyd. and $+\text{H}_2\text{O}$, -7-, and -8-arsinic acid, 2-chloro-4-methylquinoline-7-arsinic acid (I), m.p. 192° , 2-chloroquinoline-5- (II), -6-, and -8-arsinic acid, m.p. $273\text{--}276^\circ$. With $\text{OH}\cdot[\text{CH}_2]_2\text{O}\cdot[\text{CH}_2]_2\text{ONa}$ (I) and (II) give 2- β -ethoxyethoxy-4-methylquinoline-7-, m.p. 183° , and 2- β -ethoxyethoxyquinoline-5-arsinic acid, m.p. 172° , respectively. M.p. are corr.

R. S. C.

Organo-chromium compounds. Reaction products from magnesium *m*-chlorophenyl bromide and chromic chloride. F. HEIN and W. RETTER (Ber., 1938, 71, [B], 1966—1972).—The interaction of *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{MgBr}$ with anhyd. CrCl_3 gives a mixture of many compounds, some of which contain polyphenylene groups whereas others are complex oxides. Well-characterised compounds can be obtained therefrom only with great difficulty and in very small yield. The mixture is separated by MeOH into a sol. and an insol. portion. The former with KI gives salts, $\text{C}_6\text{H}_4[\text{Cr}(\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{Cl})_2]_2$ and $[\text{C}_6\text{H}_4\cdot\text{Cr}(\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{Cl})_2]_2$, which are transformed into the corresponding *reineckates*. The part insol. in MeOH contains the *substances*,



H. W.

Precipitation of magnesium phenyl bromide by pyridine and by dioxan. A. C. COPE (J. Amer. Chem. Soc., 1938, 60, 2215—2217).— $\text{C}_5\text{H}_5\text{N}$ ppts. MgPhBr less completely than does dioxan. >1.6 mol. of $\text{C}_5\text{H}_5\text{N}$ also ppts. MgPh_2 . $\text{C}_5\text{H}_5\text{N}$ indicates 78—79% of disproportionation of MgPhBr in approx. agreement with the 70—74% indicated by dioxan.

R. S. C.

Organic antimony compounds.—See B., 1938, 1231.

Partial fission of proteins. III. Gelatin. N. KONUMA (J. Biochem. Japan, 1938, 28, 51—68).—The products yielded by fractional hydrolysis of gelatin with dil. HCl or NaOH under pressure at 170° were examined for N distribution and NH_2 -acid, peptide, and diketopiperazine contents. The data are compared with those for gliadin and fibroin (cf. Kunishige, A., 1937, III, 446).

F. O. H.

Cystine content of glutenin. Polysaccharide content and reducing power of proteins and of their digest products.—See A., 1938, III, 949.

Dennstedt's simplified elementary analysis. R. DE CASTRO AYRES DO NASCIMENTO (Rev. Chim. Ind., 1938, 7, No. 75, 17—20; No. 76, 19—22).—Details of C and H determination are described.

F. R. G.

Determination of organic nitrogen. G. ROCCHI and R. DEL MONTE (Chim. e l'Ind., 1938, 20, 546—547).—The substance [*e.g.*, $\text{CaN}\cdot\text{CN}$, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CN}$, $\text{CO}(\text{NH}_2)_2$, or $\text{CS}(\text{NH}_2)_2$, or, with KMnO_4 as catalyst, uric acid or caffeine] is heated in a beaker with conc. NaOH or KOH in an autoclave at $\sim 180^\circ$, until max. pressure is reached. The gaseous products are then passed over (eventually boiling) dil. NaOH in an Erlenmeyer flask as trap, through a condenser into standard acid. This is titrated, and NH_3 evolved determined. E. W. W.

Determination of sulphur in organic substances by means of catalysts. W. RUDOLPH (Z. anal. Chem., 1938, 113, 325—326; cf. A., 1938, II, 210).—0.2 g. of the substance, 0.2 g. of MgO , and 5 c.c. of conc. HNO_3 in a micro-Kjeldahl flask are treated dropwise with 10 c.c. of fuming HNO_3 , and heated for 2—3 hr. at the b.p. The residue is dissolved in conc. HCl, evaporated to dryness, re-dissolved in HCl (1:1), and the SO_4^{2-} determined as BaSO_4 . Data for *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, sulphosalicylic acid, and tetronal are satisfactory.

L. S. T.

Determination of organic halogen. R. H. KIMBALL and L. E. TUFTS (Ind. Eng. Chem. [Anal.], 1938, 10, 530—531).—The sample (0.2—0.8 g.), weighed in a gelatin capsule, is ignited in a 15×300 mm. Pyrex combustion tube filled with $\text{Ca}(\text{OH})_2$, and held horizontally in a short-tube furnace in such a way that the tube above the capsule is heated to redness before ignition of the sample, which takes 45—60 min. After cooling, the ignited mixture is dissolved in dil. HNO_3 and titrated directly by Caldwell and Moyer's modification of Volhard's method (A., 1935, 316).

F. N. W.

Selenium dioxide as an oxidising agent in organic chemistry. K. KRATZL (Österr. Chem.-Ztg., 1938, 41, 340—344).—A summary. The sp.

action of SeO_2 in oxidising CH_2 adjacent to CO or CHO , or near to a double linking, is discussed. With liquids the reaction is generally carried out without a solvent, an excess of SeO_2 being used. With solids oxidation is carried out in an indifferent solvent (Et_2O , PhMe , xylene, EtOH , or Ac_2O) under reflux. Traces of H_2O often hinder oxidation. The oxidation of double linkages by SeO_2 at high temp. is also discussed. The high cost of SeO_2 is offset by the high yields obtained, and the fact that the Se remaining may be recovered and reconverted easily into SeO_2 .

J. W. S.

Application of drop analysis to the investigation of medicinal materials. IV. Detection of chloroform. O. FREHDEN and K. FÜRST (Mikrochim. Acta, 1938, 3, 133—135).—A few drops of the solution under test are treated with 2 drops of 20% NaOH and 1 drop of conc. NH_3 . After a few min. the solution is boiled, cooled, and then acidified with 20% H_2SO_4 , the vapours evolved being tested for HCN . The test-papers used are impregnated either with $\text{Cu}(\text{OAc})_2$ + benzidine acetate or with 2:7-diaminofluorene.

J. W. S.

Determination of ethylene dibromide. M. W. BRENNER and G. L. POLAND (Ind. Eng. Chem. [Anal.], 1938, 10, 528—529).—The sample (25—136 mg.) is refluxed (180 min.) with 10 c.c. of 20—30% aq. KI and 50 c.c. of EtOH , and the liberated I titrated with 0.01N- or 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$ after addition of 140 c.c. of H_2O . Although the method gives only 95% recovery, the results obtained are reproducible and in the absence of interfering substances a correction may be applied.

F. N. W.

Determination of alcohols in pharmaceutical liquids. K. BAMBACH (Ind. Eng. Chem. [Anal.], 1938, 10, 541—543).—Use is made of Foulk's chain hydrometer to measure the d of EtOH - H_2O mixtures. d of mixtures containing 0—52% EtOH are recorded from 15.56° to 34°.

F. N. W.

Determination of glycerol in aqueous solution. O. JUHLIN (Z. anal. Chem., 1938, 113, 339—340).—The reaction $\text{C}_3\text{H}_5(\text{OH})_3 + \text{Br}_2 = \text{CO}(\text{CH}_2\text{OH})_2 + 2\text{HBr}$ is utilised for dil. and conc. solutions. A wt. of solution corresponding with 0.002—0.004 g. of pure glycerol is neutralised (Me-orange) with 0.1N- KOH and allowed to react for 15 min. with 10 c.c. of 0.1% Br - H_2O in a 500-c.c. Erlenmeyer flask with its stopper moistened with aq. KI . 10 c.c. of 10% KI and 50—100 c.c. of H_2O are added, and the liberated I is titrated with 0.02N- $\text{Na}_2\text{S}_2\text{O}_3$ (starch).

L. S. T.

Colorimetric micro-determination of diacetyl. E. A. PRILL and B. W. HAMMER (Iowa State Coll. J. Sci., 1938, 12, 385—395).—A slightly acidified (food) product containing Ac_2 is distilled (details given) in steam in CO_2 and the distillate is collected in aq. NH_2OH - NaOAc . The distillate is heated at 85° for 1 hr. and excess of NH_2OH removed with K_2HPO_4 - COMe_2 . Addition of NH_3 (d 0.90) and Rochelle salt, followed by FeSO_4 , gives a rose-red colour which is compared with a standard. The determinations agree with the gravimetric method within 4.5%. CHO - CO_2H , AcCO_2H , COMePr , and AcCHO give colours under similar conditions.

J. L. D.

Determination of lactic acid. P. E. GALVÃO, C. H. FLORENCE, and J. PEREIRA (Arq. Inst. Biol., 1938, 9, 39—50).—A modification of the method of Friedemann *et al.* (A., 1927, 800) in which, *inter alia*, temp. of the condenser-water is kept slightly above the b.p. of MeCHO .

S. O.

Drastic saponification method for difficultly saponifiable esters. W. E. SHAEFER and J. PICCARD (Ind. Eng. Chem. [Anal.], 1938, 10, 515—517).—The sample is hydrolysed by refluxing (16 hr.; 150°) with 10 c.c. of a solution of NaOMe in MeOH -cyclohexanol (I) [9.3 g. of Na in 500 c.c. of (I) and 250 c.c. of abs. MeOH] in moist N_2 , after preliminary removal of the MeOH (0.5 hr.; 150° without reflux). The method is accurate to 1%, and has been applied to the quant. saponification of abietic esters. It cannot be used for the analysis of glycerol derivatives.

F. N. W.

Determination of sugar by means of copper reduction methods. T. YOSHIDA, Y. IWATA, and K. YAMAFUJI (Enzymologia, 1938, 2, 342—343).—Details are given of modifications in the use of Fehling's and Luff's solutions in the determination of reducing sugars in the presence of sucrose.

P. G. M.

Relationships between the determination of pentosans and lignin. R. S. HILPERT and H. MEYBIER (Ber., 1938, 71, [B], 1962—1965).—Furfuraldehyde (I) is converted by acids into non-volatile products the amount of which depends on the time during which the reactants are in contact. These products are very similar to those derived from acid and sugars, pointing thus to the possibility that (I) is first produced. Determination of lignin (II) depends also on a treatment with conc. HCl . The residues from the determination of pentosans (III) in pine, red and white beech, and rye straw have C and H contents within the limits determined for (II) but the OMe content is lower. That which is actually accomplished in the determination of (III) is the measurement of the amount of (I) which can be volatilised. With varied woods high % of (I) is accompanied by low % of (II) and vice versa, and the observed differences may depend solely on the rate at which (III) are converted into insol. products.

H. W.

Perchloric-acetic acid method of amino-acid titration. G. TOENNIES and T. P. CALLAN (J. Biol. Chem., 1938, 125, 259—268).—An improved HClO_4 method of determining NH_2 -acids gives results in agreement with the formol method. Cystine, however, behaves anomalously.

R. S. C.

Photometric determination of cystine, cysteine, ascorbic acid, and related compounds with phosphotungstic acid. (MISS) B. KASSELL and E. BRAND (J. Biol. Chem., 1938, 125, 115—129).—Cystine, cysteine, and ascorbic acid alone or together are determined by photometric measurement of the blue colour developed with phospho-18-tungstic acid. Applications to urine, lactalbumin, and reduced lactalbumin (I), and a micro-modification (10—20 mg. of protein) are described. 75% of the cystine in (I) is present as cysteine.

R. S. C.

Direct determination of creatine.—See A., 1938, III, 972.

Oxidations with hypoiodite. I. Phenols.
Determination of adrenaline and tyrosine. K. H. SLOTTA and K. NEISSER [with L. MANGINELLI] (Ber., 1938, 71, [B], 1611—1616).—The neutral or acid solution of the phenol is mixed with a known vol. of standard I solution. NaOI is formed in the solution by addition of NaOH; after a suitable interval the solution is acidified and the liberated I is titrated with $\text{Na}_2\text{S}_2\text{O}_3$. Solutions of *o*- and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$ are immediately decolorised when made alkaline and CHI_3 separates after some time, whereas those of *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ become pink and the formation of CHI_3 cannot be detected. 1 : 3 : 5- $\text{C}_6\text{H}_3(\text{OH})_2$ resembles *m*- $\text{C}_6\text{H}_4(\text{OH})_2$. The intermediate formation of quinones is established by the isolation of quinhydrone by use of a suitable amount of I. Since PhOH gives *o*- $\text{C}_6\text{H}_4\text{I}\cdot\text{OH}$ and 2 : 4 : 6- $\text{C}_6\text{H}_2\text{I}_3\cdot\text{OH}$ it is probable that with dihydric phenols *ortho* substitution follows the formation of quinone; this view is strengthened by the observation that *cyclohexanone* requires exactly 2 I. The probability that further oxidation in the alkaline solution is accompanied by fission between the Cl-CO group and the vicinal C is strengthened by the observation that *o*- and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$ require 10 I and 12 I respectively. The quantities of CHI_3 formed as final product of the oxidation indicate that the change occurs also in other, unexplained directions. $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ is indifferent towards OI, showing that a side-chain, in itself active, does not influence the oxidation of the aromatic nucleus. The universal applicability of the method to quinones with an α -H is shown by the behaviour of Na naphtha-1 : 2-quinone-4-sulphonate. The application of the method to the determination of adrenaline and tyrosine is described. H. W.

Modification of the Gerngross-Voss-Herfeld reaction, permitting the photometric micro-determination of tyrosine, tyramine, and other para-substituted phenols. A. MACIAG and R. SCHOENTAL (Mikrochem., 1938, 24, 250—252).—The colour developed in this reaction (A., 1933, 407) is stabilised by immediate addition of saturated aq. $(\text{NH}_4)_2\text{SO}_4$, $\text{Fe}_2(\text{SO}_4)_3$, and boiling. The coloration so obtained obeys Beer's law, and permits the micro-colorimetric determination of tyramine, tyrosine, etc. E. W. W.

Determination of the tocopherols in various initial materials. P. KARRER and K. KELLER (Helv. Chim. Acta, 1938, 21, 1161—1169).— α -Tocopherol (I) can be sharply titrated potentiometrically with AuCl_3 in 80% EtOH; β -tocopherol (II) (neotocopherol) behaves similarly, 3 mols. of the substances requiring 2 mols. of AuCl_3 . Under the experimental conditions carotene and other carotenoids reduce AuCl_3 and hence may be present, at most, in traces. The unsaponifiable matter from wheat-germ, maize-germ, linseed, olive, sesamé, palm, and cottonseed oil contains so little carotenoid that no error is introduced into the titration result, but a correction must be applied to that from the oil of cabbage lettuce. The results are the sum of (I) and

(II) with γ -tocopherol if present. Since (I) is considerably more active biologically than (II) a complete parallelism between chemical and biological assay can be expected only if the ratio of (I) : (II) is const. for all natural sources. Whether or not this is the case cannot be decided at present. In wheat-germ oil the tocopherols are not present as esters. β -Carotene gives a well-defined titration curve with AuCl_3 , 1 mol. requiring nearly 8 equivs. of oxidant. H. W.

Two-step oxidation-reduction of lapachol, lomatiol, and related compounds. E. S. HILL (J. Amer. Chem. Soc., 1938, 60, 1990—1994).—A technique for titrating lomatiol, hydrolomatiol, lapachol, hydroxyhydrolapachol, and *iso*- β -lapachol reductively from p_H 7.1 to p_H 14.3 is described. The results show two-stage reduction and indicate semiquinone formation to a max. of 61% at p_H 14.24. R. S. C.

Modification of Pauly's reaction, in relation to the micro-colorimetric (photometric) determination of glyoxalines (histamine). A. MACIAG and R. SCHOENTAL (Mikrochem., 1938, 24, 243—250).—Immediate addition of EtOH stabilises the red colour obtained in Pauly's (dialzo-)reaction, and permits the micro-colorimetric determination of histamine (or histidine, tyrosine, or tyramine). There is, however, no satisfactory chemical method for determining blood-histamine. E. W. W.

Microchemical reactions of barbiturates. J. P. L. VILLAMIL (Arch. Med. Legal, 1933, 6, 366—377).—Veronal, luminal, and gardinal in concns. >0.05% give cryst. ppts. with Ag_2CO_3 in NH_3 . S. O.

Semimicro-conductometric determination of nicotine. R. RIPAN-TILICI and F. CRISTEA (Z. Unters. Lebensm., 1938, 76, 44—51).—Nicotine is determined by titration with silicotungstic acid (I), the end-point being indicated by an inflexion on the conductivity-(I) curve. For the necessary acidification of the (I) solution AcOH or tartaric, rather than a mineral, acid should be used. E. C. S.

Aminometry of alkaloids. II. Amines, alkaloids, and alkaloid-containing drugs. R. DIETZEL and W. PAUL [with O. RUPPRECHT and R. SIBER] (Arch. Pharm., 1938, 276, 408—409).—The authors' method (A., 1936, 219) is improved by using CHCl_3 as solvent and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ and $(\text{CH}_2)_6\text{N}_4$ as standard acid and base, respectively, and by working in open vessels. It is applicable to aliphatic ($>\text{C}_4$), some aromatic, and the stronger heterocyclic bases, including many alkaloids. It fails for hyoscyamine in belladonna leaves, probably owing to hydrolysis. R. S. C.

Application of Reinecke salt in the determination of some alkaloids. H. SCHMIDT-HEBREL and P. A. BENAVIDES (Pharm. Zentr., 1938, 79, 526—528).—0.5 c.c. of 0.1N- H_2SO_4 is added to 10 c.c. of a 1% solution of the alkaloid before addition of excess of a cold saturated solution of Reinecke salt, and after 1 hr. the ppt. is washed with ice- H_2O , dried, and ignited. Accurate results were obtained with strychnine, atropine, morphine, papaverine, codeine, and cocaine. E. H. S.

A., II.—Organic Chemistry

DECEMBER, 1938.

Suggested nomenclature for heterogeneous acyclic chain compounds. R. RAMBAUD (Bull. Soc. chim., 1938, [v], 5, 1385—1392). A. T. P.

Mercury-photosensitised decomposition of ethane.—See A., 1938, I, 632.

Kinetics of the decomposition reactions of the lower paraffins. II. *iso*Butane.—See A., 1938, I, 627.

Polymerisation of ethylene with compounds of aluminium as catalyst. F. C. HALL and A. W. NASH (J. Inst. Petroleum Tech., 1938, 24, 471—495; cf. A., 1938, II, 7).—The catalytic polymerisation reactions of C_2H_4 are reviewed with particular reference to the use of $AlCl_3$ as catalyst. If a mixed $Al-AlCl_3$ catalyst is used, the reaction products consist of $Al-Et$ derivatives and polymeric hydrocarbons of high b.p., and the residual and distillate lubricating oils have much higher η than those produced using $AlCl_3$ alone. The optimum vals. are obtained for oils from reaction at 200° . The secondary cracking action of $AlCl_3$ on the oils produced may be completely inhibited by Al or Mg ; Zn is less efficient. Above 200° , the polymerisation is affected by $Al-Et$ derivatives, and high yields of Δ^a -butene, hexene, or octene can be obtained using either $AlEt_2Cl$ or $AlCl_3-Al$ catalysts. The reaction is in accordance with the mechanism of free alkyl radicals proposed by Taylor and Jones (A., 1930, 757) and it is suggested that the free radicals originate from thermal decomp. of $Al-Et$ compounds.

J. D. R.

Preparation of alkenes by the thermal decomposition of alkyl acetates. J. P. WIBAUT and A. J. VAN PELT, jun. (Rec. trav. chim., 1938, 57, 1055—1058).—Thermal decomp. of the acetates of CH_3CH_2OH , $n-C_7H_{15}OH$, $CHPr^{\beta}_2OH$, and $CHPr^{\beta}Bu^{\gamma}OH$ over glass wool at $440-525^\circ$ gives yields of 75—88% of Δ^{β} -pentene, Δ^a -heptene, $\beta\delta$ -dimethyl- and $\beta\delta\delta$ -trimethyl- Δ^{β} -pentene, respectively.

J. D. R.

Lengthening carbon chains by three units. Assay of primary bromides from the addition of hydrogen bromide. A. P. KOZACIK and E. E. REID (J. Amer. Chem. Soc., 1938, 60, 2436—2438).—The reactions, $RBr \rightarrow MgRBr \rightarrow CH_2R-CH:CH_2 \rightarrow CH_2R-CH_2-CH_2Br$, are used to lengthen C chains by 3 units. Δ^a -Tridecene, b.p. $102-103^\circ/10$ mm., m.p. -13° , Δ^a -pentadecene, b.p. $127.5-128.5^\circ/10$ mm., m.p. -2.8° , Δ^a -heptadecene, b.p. $155.4-156.4^\circ/10$ mm., m.p. 11.2° , and Δ^a -nonadecene, b.p. $177^\circ/10$ mm., m.p. 21.7° , Δ^a -butenyl- and Δ^a -hexenyl-benzene are thus prepared. The addition of HBr (Kharasch *et al.*,

A., 1937, II, 479) gives 41, 60, 12, 3, 82, and 65%, respectively, of primary bromide, as estimated by condensation with *p*-substituted phenols in $KOH-EtOH$ at 70° for the alkyl or with $\beta-C_{10}H_7OH$ for the aralkyl bromides and comparison with authentic samples. The following are reported: *quinol octyl*, m.p. 60° , *decyl*, m.p. 63.8° , *dodecyl*, m.p. 65.2° , and *tetradecyl*, m.p. 67.4° , *n-nonyl ether*; *quinol octyl*, m.p. 60.6° , *decyl*, m.p. 69.8° , and *dodecyl*, m.p. 71.8° , *n-undecyl ether*; *quinol butyl*, m.p. 62.8° , *octyl*, m.p. 65.2° , and *decyl*, m.p. 67.6° , *n-tridecyl ether*; *quinol dodecyl pentadecyl ether*, m.p. 75.6° ; *p-chloro-*, m.p. 48° , and *p-iodo-phenol n-pentadecyl ether*, m.p. 57.2° ; *quinol CH₂Ph n-heptadecyl ether*, m.p. 91.8° ; *p-chloro-*, m.p. 54.2° , and *p-iodo-phenyl n-heptadecyl ether*, m.p. 64° ; *Ph n-nonadecyl ether*, m.p. 56° . R. S. C.

Preparation of some lower alkyl chlorides from the corresponding alcohols using zinc chloride and concentrated hydrochloric acid. A. M. WHALEY and J. E. COPENHAVER (J. Amer. Chem. Soc., 1938, 60, 2497—2498).—Prep. of Pr^aCl , Bu^aCl , and *sec*- $BuCl$ from the alcohol by $ZnCl_2-HCl$ is improved to give 70—83% yields. R. S. C.

Fluorinated derivatives of propane. II. A. L. HENNE and E. C. LADD (J. Amer. Chem. Soc., 1938, 60, 2491—2495; cf. A., 1938, II, 2).—Fluorination (SbF_3Cl_2 or SbF_3-SbCl_5) of C_3Cl_8 , $C_2Cl_5-CHCl_2$ (I), and $CHCl(CCl_3)_2$ is complicated, as the starting materials may cleave to olefines, which absorb more F. Fission of the fluorinated products does not occur, as no products derived from fluorinated olefines are obtained. (I) (obtained from C_2Cl_4 , $CHCl_3$, and $AlCl_3$), b.p. $163-166^\circ/90$ mm., gives $\alpha\alpha\beta\gamma\gamma$ -hexachloro- α -fluoropropane (II), a glass, b.p. 210° , $\alpha\beta\beta\gamma\gamma$ -pentachloro- $\alpha\alpha$ -difluoropropane (III), a glass, b.p. 168.4° , $\alpha\beta\gamma\gamma$ - or $\alpha\beta\beta\gamma$ -tetrachloro- $\alpha\alpha\beta$ - or $\alpha\alpha\gamma$ -trifluoropropane, a glass, b.p. 129.8° , $(CCl_2)_2$, CCl_3-CCl_2F , $(CCl_2F)_2$, and C_2Cl_6 . C_3Cl_8 [prep. from (I) by treatment with $KOH-MeOH$, followed by Cl_2 at $<50^\circ$ in light] gives $\alpha\alpha\beta\beta\gamma\gamma$ -heptachloro- α -fluoropropane (IV), b.p. 236.8° , m.p. 97° , $\alpha\alpha\beta\beta\gamma\gamma$ -hexachloro- $\alpha\gamma$ -difluoropropane (V), b.p. 194.2° , m.p. 29.8° , and (?) $\alpha\alpha\beta\beta\gamma$ -pentachloro- $\alpha\gamma\gamma$ -trifluoropropane, m.p. -4.9° , b.p. 152.3° . $CHCl(CCl_3)_2$ (prep. from C_2HCl_3 , CCl_4 , and $AlCl_3$), b.p. $126-132^\circ$, gives $\alpha\alpha\alpha\beta\gamma\gamma$ -hexachloro- γ -fluoropropane (VI), a glass, b.p. 207° (decomp.), and $\alpha\alpha\beta\beta\gamma\gamma$ -pentachloro- $\alpha\gamma$ -difluoropropane (VII), a glass, b.p. 167.4° . With Zn (VI) gives only $ZnCl_2$, with Cl_2 in light yields (IV), and with $KOH-EtOH$ gives mixed olefines, converted by Cl_2 into (IV). With Zn (II) gives only $ZnCl_2$, with Cl_2 gives (V), and with KOH gives a pure olefine, which yields (IV). The F_2 -compounds are also obtained from the F_1 -com-

pounds, showing that one F is terminal. With Cl_2 in light (III) gives $\text{C}_2\text{Cl}_5\cdot\text{CClF}_2$. With Zn (VII) gives only ZnCl_2 and with Cl_2 gives (V). $\alpha\alpha\beta\beta\gamma$ -Hexachloro- $\gamma\gamma$ -difluoro-, m.p. $50\cdot8^\circ$, b.p. $193\cdot4^\circ$, $\alpha\alpha\gamma\gamma\gamma$ -hexachloro- $\beta\beta$ -difluoro-, m.p. $-12\cdot9^\circ$, b.p. $194\cdot2^\circ$, and $\alpha\alpha\gamma\gamma$ -pentachloro- $\beta\beta\gamma$ -trifluoro-propane, m.p. $<-80^\circ$, b.p. $154\cdot5^\circ$, are described. R. S. C.

Isomerisation during the preparation of *n*-amyl chloride. F. C. WHITMORE, F. A. KARNATZ, and A. H. POPKIN (J. Amer. Chem. Soc., 1938, 60, 2540—2542).— $n\text{-C}_5\text{H}_{11}\cdot\text{OH}$ and $\text{ZnCl}_2\text{-HCl}$ give 57% of $n\text{-C}_5\text{H}_{11}\text{Cl}$ with 10% of β - + γ -Cl-compounds. $n\text{-C}_5\text{H}_{11}\text{Cl}$ (obtained in 80% yield by $\text{SOCl}_2\text{-C}_5\text{H}_5\text{N}$) and $\text{ZnCl}_2\text{-HCl}$ give only 3% of β - + γ -Cl-compounds. Rearrangement thus occurs largely before esterification. Bu^oOH and $\text{HBr-H}_2\text{SO}_4$ give only Bu^aBr . R. S. C.

Preparation and properties of β - and γ -chloropentanes. F. C. WHITMORE and F. A. KARNATZ (J. Amer. Chem. Soc., 1938, 60, 2536—2538).— β - (I), b.p. $96\cdot84\text{--}96\cdot86^\circ$, m.p. -137° to -139° , and γ -chloropentane, b.p. $97\cdot76\text{--}97\cdot82^\circ$, m.p. -105° to -106° , are best obtained from the alcohols by $\text{SOCl}_2\text{-C}_5\text{H}_5\text{N}$; gaseous HCl at room temp. gives mixtures. The chlorides are equilibrated [80% of (I)] by $\text{ZnCl}_2\text{-HCl}$ at room temp., but are unchanged by heating alone at 100° . R. S. C.

Pinacolyl chloride from the chlorination of neohexane [$\beta\beta$ -dimethyl-*n*-butane]. F. C. WHITMORE, H. I. BERNSTEIN, and L. W. MIXON (J. Amer. Chem. Soc., 1938, 60, 2539).— CMe_2EtCl and MgMeCl in Bu^a_2O give 36—39% of $\beta\beta$ -dimethyl-*n*-butane, b.p. $49\cdot5^\circ/730\text{ mm.}$, which with Cl_2 at -18° gives amongst other products 11% of pinacolyl chloride [β -chloro- γ -methyl-*n*-butane], b.p. $109\cdot9^\circ/734\text{ mm.}$, m.p. $-0\cdot9^\circ$. This is a stable *sec.* chloride, behaving normally with AgNO_3 and giving by way of its Mg compound a HgCl derivative, m.p. $88\cdot5\text{--}90^\circ$. R. S. C.

Exchange of deuterium between methyl alcohol and water.—See A., 1938, I, 620.

Fractional distillation of mixtures of constant b.p. R. WRIGHT (J.C.S., 1938, 1720—1721).—The effect on the composition of distillate of adding $\text{CH}_2\text{Ph}\cdot\text{OBz}$, liquid paraffin, palmitic and stearic acids, sucrose, K_2CO_3 , and KOH to the azeotropic mixture of Pr^oOH and H_2O has been determined. Addition of KOH permits a good yield of pure Pr^oOH to be obtained after three distillations. Improved separation of EtOH from H_2O is obtained by distilling the mixture with CaO and liquid paraffin. E. S. H.

Alkyl chlorides obtained from β -ethyl-*n*-butanol. F. C. WHITMORE and F. A. KARNATZ (J. Amer. Chem. Soc., 1938, 60, 2533—2536).— $\text{CHEt}_2\cdot\text{CH}_2\cdot\text{OH}$ (I) with $\text{ZnCl}_2\text{-HCl}$ gives 35—40% of CMeEt_2Cl , b.p. $69\cdot5^\circ/160\text{ mm.}$, 5—10% each of CHMeBu^aCl , $\text{CMe}_2\text{Pr}^a\text{Cl}$, b.p. $63\cdot5\text{--}64^\circ/160\text{ mm.}$, and *sec.*- CHMeBuCl , and 1—5% each of $\text{CHEt}_2\cdot\text{CH}_2\text{Cl}$, b.p. $88^\circ/225\text{ mm.}$, CHEtPr^aCl , and CHMeBu^bCl . Rearrangement occurs at least mainly before esterification, as 70% of $\text{CHEt}_2\cdot\text{CH}_2\text{Cl}$ (obtained in 82% yield by SOCl_2) is recovered after treatment with $\text{ZnCl}_2\text{-HCl}$. A mechanism based on the author's

theories is expounded. γ -Methylpentan- β -, m.p. $145\text{--}146^\circ$, and hexan- γ -one-2 : 4-dinitrophenylhydrazone, m.p. $146\cdot5\text{--}148\cdot5^\circ$, α -methyl- α -ethyl-*n*-butyranilide, m.p. $87\cdot5\text{--}89^\circ$, and β -ethylvalerianilide, m.p. $83\text{--}84^\circ$, are incidentally described. R. S. C.

Catalytic reductions under high pressures. L. PALFRAY and S. SABATEY (Bull. Soc. chim., 1938, [v], 5, 1423—1425; cf. A., 1936, 446, 729).—Hydrogenation (Ni) is carried out in 500—1000-g. quantities, and details are recorded of the prep. of: dimethyloctanol, b.p. $106^\circ/12\text{ mm.}$; di-, b.p. $96\text{--}97^\circ/14\text{ mm.}$ and tetra-, b.p. $87^\circ/15\text{ mm.}$, -hydroxinalol; dihydrocoumarin, b.p. $145^\circ/13\text{ mm.}$; dihydro-, b.p. $121^\circ/14\text{ mm.}$ (Ac derivative, b.p. $155^\circ/17\text{ mm.}$), and (?) octahydro-, b.p. $108^\circ/16\text{ mm.}$, -isoeugenol; tetra-, b.p. $120\text{--}121^\circ/13\text{ mm.}$ (picrate, m.p. 142°), and deca-, m.p. 27° , b.p. $89\text{--}90^\circ$ (picrate, m.p. 159°), -hydroquinoline; carvomenthol, b.p. $100\text{--}104^\circ/12\text{ mm.}$; menthol from thymol and *Mentha pulegium*. A. T. P.

Derivatives of the aliphatic glycols. IV. G. M. BENNETT and H. GUDGEON (J.C.S., 1938, 1679—1681).—An improved method for the prep. of aliphatic glycols with 12, 14, or 16 C atoms is described. Reduction (Na-EtOH) of $\text{CO}_2\text{Et}\cdot[\text{CH}_2]_{16}\cdot\text{CO}_2\text{Et}$ yields octadecamethylene glycol (I), m.p. $97\text{--}98^\circ$. Interaction of the appropriate glycol and HCl yields μ -chlorododecyl alcohol, m.p. 28° , b.p. $134^\circ/1\text{ mm.}$ (phenylurethane, m.p. 66°), and ξ -chlorotetradecyl alcohol, m.p. $37\text{--}38^\circ$, b.p. $156\text{--}160^\circ/4\text{ mm.}$ (phenylurethane, m.p. 68°). The latter is also formed (with $\alpha\xi$ -dichlorotetradecane, m.p. 40°) from the glycol and NPhMe_2 with SOCl_2 in C_6H_6 ; by this process the C_{16} and C_{18} glycols yield π -chlorohexadecyl alcohol, m.p. 43° , and σ -chloro-octadecyl alcohol, m.p. $53\text{--}54\cdot5^\circ$ (phenylurethane, m.p. 77°), $\alpha\pi$ -dichlorohexadecane, m.p. 47° , and $\alpha\sigma$ -dichloro-octadecane, m.p. 54° , being formed as by-products. J. D. R.

Warning against ether explosions. J. TANDBERG (Chem.-Ztg., 1938, 62, 731—732).—Warning is given against the danger of explosion with Et_2O which contains peroxides, which are formed when the Et_2O had been kept for a long time in sunlight or has been agitated with air. The presence of peroxides can be detected with $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$, KI + acid, or TiSO_4 . J. W. S.

Kinetics of thermal decomposition of propylene oxide.—See A., 1938, I, 627.

Claisen's method for the preparation of ethers of hydroxymethylene compounds. K. von AUWERS (Ber., 1938, 71, [B], 2082).—The $\cdot\text{CH}\cdot\text{OH}$ compound is boiled in COMe_2 or dried technical COMeEt with an equimol. amount of ignited, finely-divided K_2CO_3 and somewhat $>$ a mol. amount of alkyl halide until the change is complete (usually a working day). Separation of the salt which is produced is completed by the addition of Et_2O , after which the mixture is filtered and the filtrate rectified in a vac. The yields are generally almost quant. Only $\text{CH}\cdot\text{OH}$ compounds are smoothly converted into *O*-ethers by this process. $\alpha\gamma$ -Diketones and β -CO-esters afford *C* derivatives. H. W.

Organic peroxides. V. *tert*-Butyl hydrogen peroxide. N. A. MILAS and S. A. HARRIS (J. Amer. Chem. Soc., 1938, 60, 2434—2436; cf. A., 1934, 778).—When Bu^oOH is treated with 30% aq. H₂O₂, then shaken successively with anhyd. Na₂SO₄, MgSO₄, and HPO₃, and fractionated over MgSO₄ or HPO₃, Bu^o H peroxide, b.p. 38—38.5°/18 mm., m.p. —13.5°, is obtained; it is unusually stable. HCl does not give Bu^oCl unless FeCl₂ is also present. It decomposes only very slowly at room temp., even in presence of alkali, pure liver catalase, or horse-radish peroxidase (unless an acceptor, e.g., pyrogallol, is added), or Pd-black (unless Na₂HPO₄ is added).

R. S. C.

β-Aminoethylsulphuric acid, an irregular ampholyte. D. B. ROLLINS and H. N. CALDERWOOD (J. Amer. Chem. Soc., 1938, 60, 2312—2314).—The acid is prepared in theoretical yields from OH·[CH₂]₂·NH₂ and H₂SO₄ by a modified procedure. The mol. wt., determined by titration and by cryoscopy, agrees with that for the simple formula. The compound exhibits many properties common to aliphatic NH₂-acids. The ester linking is very resistant to hydrolysis.

E. S. H.

Photolysis of mercaptans.—See A., 1938, I, 633.

Addition of sulphur, hydrogen sulphide, and mercaptans to unsaturated hydrocarbons. S. O. JONES and E. E. REDD (J. Amer. Chem. Soc., 1938, 60, 2452—2455).—When passed over pyrites at 350°, C₂H₄ gives H₂S, EtSH, and 1% of thiophene, but when bubbled through S at 325° gives much H₂S with 3% of EtSH and a little CS₂ and Et₂S₂. When bubbled through Et₂S₄ at 150°, C₂H₄ gives EtSH 5, Et₂S₂ 18, and (CH₃)₂S 1%; C₂H₆ gives Pr^oSH 6, Pr^oS₂ 20, and (·CHMe·CH₃)S 15%; Δ^o-C₇H₁₄ gives C₅H₁₁·CHMe·SH 20%; Δ^o-C₈H₁₆ gives C₆H₁₃·CHMe·SH (I) 19%, and cyclohexene gives 8% each of cyclohexyl mercaptan (II) and the cyclic sulphide. H₂S or RSH alone does not add to olefines. With H₂S and S at 180° C₂H₄ gives EtSH 11 and Et₂S₂ 80%, C₃H₈ gives Pr^oSH 7 and Pr^oS₂ 90%, CH₂:CMe₂ gives Bu^oSH 23 and Bu^oS₂ 6%, Δ^o-C₈H₁₆ gives (I) 19 and (C₆H₁₃·CHMe)₂S₂ 35%, and cyclohexene gives (II) 7 and dicyclohexyl sulphide 5%. S catalyses the addition of mercaptans to the *sec*. C; peroxides (ascaridole or traces formed on storage) catalyse "abnormal" addition to the primary C. The following are obtained from the mercaptan by (a) the olefine and (b) the bromide: *Ph undecyl*, m.p. 33.8°, *tridecyl*, m.p. 43.9°, *pentadecyl*, m.p. 51.1°, *heptadecyl*, m.p. 57.6°, and *nonadecyl*, m.p. 62.4°, *sulphide*; *p-tolyl undecyl*, m.p. 29.8°, *tridecyl*, m.p. 43.9°, *pentadecyl*, m.p. 48.8°, *heptadecyl*, m.p. 56°, and *nonadecyl*, m.p. 61°, *sulphide*; β-C₁₀H₇ *undecyl*, m.p. 46.8°, *tridecyl*, m.p. 54.6°, *pentadecyl*, m.p. 61°, *heptadecyl*, m.p. 66.2°, and *nonadecyl*, m.p. 71.2°, *sulphide*; *undecyl lauryl sulphide*, m.p. 37.2°, *lauryl tridecyl*, m.p. 39.8°, *pentadecyl*, m.p. 49.2°, *heptadecyl*, m.p. 53.6°, and *nonadecyl*, m.p. 53.2°, *sulphide*.

R. S. C.

Heavy formic and acetic acids.—See A., 1938, I, 554.

Pyrolysis of esters. C. D. HURD and F. H. BLUNCK (J. Amer. Chem. Soc., 1938, 60, 2419—

2425).—Ease of pyrolysis of esters is in the order, *tert*. > *sec*. > primary alkyl. PhOAc and CH₂Ph·CO₂Me are much more stable than are AlkOAc, no change occurring at 535°. At 360—430° Bu^oOAc gives only CH₂:CMe₂ and AcOH, the olefine and AcOH in this and other cases being formed in equiv. amounts. At 435—545° CH₂Ph·CO₂Et gives C₂H₄ and CH₂Ph·CO₂H, but at 625° gives CH₂Ph·CO₂H 55, C₂H₄ 78, PhMe 22, and CO₂ 21%, some of the acid decomposing. Pr^oOAc gives C₂H₆ and AcOH, but at 460° also MeCHO 4, COMe₂ 3, and CO 12%. EtOAc gives C₂H₄ and AcOH with, at 550°, MeCHO 9, CH₂O 6, Ac₂O 0.5, CH₄ 8, H₂ 4, CO 1%, and CH₂:CO a trace. Bu^oOAc gives CH₂:CMe₂, AcOH, and small amounts of Pr^oCHO, CO, and CH₄. At 625° PhOAc gives 84% of CH₂:CO and PhOH. CH₂Ph·CO₂Me at 625° undergoes a complex decomp., yielding PhCHO >71, PhMe >49, CO 92, CH₂O 25, C₂H₄ 29, H₂ 27, CH₄ 15, CO₂ 12, and an acid 4%. A reaction involving a cyclic H bridge is postulated to explain the low-temp. decomp., but a chain reaction involving free radicals occurs at higher temp. Formation of CHPh is necessary to account for the PhCHO produced.

R. S. C.

Alcoholysis of esters. II. S. L. LETSCHUK and A. N. POPOVA (Prom. Org. Chim., 1938, 5, 628—631).—The reaction ROAc + BuOH → BuOAc + ROH is more actively catalysed by HCl when R = bornyl, and by KOH when R = Me.

R. T.

Interaction of sodamide with salts of formic acid.—See A., 1938, I, 628.

Reaction of some anhydrous [metallic] chlorides with anhydrous acetic acid and formic acid.—See A., 1938, I, 633.

Derivatives of (SNH)₄.—See A., 1938, I, 603.

Preparation of fatty acids containing deuterium. W. E. VON HEYNINGEN, D. RITTENBERG, and R. SCHOENHEIMER (J. Biol. Chem., 1938, 125, 495—500).—*Deuteropalmitic acid*, m.p. 62.5°, has been prepared by the exchange action of D₂SO₄ on palmitic acid; this occurs only at α-C. *Deuterolauric acid*, m.p. 45.2°, has been prepared by heating K laurate in presence of PtO₂ with D₂O and then acidifying. The D thus introduced is not removed by treatment with alkali or mineral acids at elevated temp.

T. F. D.

Reduction of organic compounds by atomic hydrogen. I. Reduction of oleic, elaidic, and linoleic acids to stearic acid. E. V. ZAPPI and H. DEGIORGI (Anal. Asoc. Quím. Argentina, 1938, 26, 33—40).—Apparatus for reduction with H adsorbed in a W filament is described. Oleic and elaidic acids are reduced with equal ease, but linoleic acid gives only a little stearic acid, the major part being polymerised.

F. R. G.

Elaidinisation of oleic acid and *cis-trans* isomerism. S. H. BERTRAM (Öle, Fette, Wachse, 1938, 3, No. 7, 1—4).—The elaidinisation of oleic acid is a reversible reaction reaching equilibrium at 1 mol. oleic acid (I): 2 mols. elaidic acid (II), whatever catalyst or reaction temp. be employed. It is considered that Se, as catalyst, forms an

unstable additive compound with 3 mols. of (I) or (II), which subsequently decomposes to yield the equilibrium mixture of the two acids. This view is supported by determinations of the velocities of elaidinisation and of the reverse reaction, and calculations of the reaction consts., which indicate that either reaction is termol. The author's reasons for assigning the *trans*-configuration to oleic acid are recapitulated.

E. L.

Definition of tautomerism. K. A. JENSEN (J. pr. Chem., 1938, [ii], 151, 177—184).—The possible forms of the acetoacetic ion $\text{Me}\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ and $\text{Me}\cdot\text{C}\ddot{\text{O}}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ are distinguished from one another only by the distribution of electrons and are mutually transformable without altering the positions of the at. nuclei; they are therefore mesomeric. There is only one ion which is intermediate in form between the above structures. This mesomerism explains the production of *C*- and *O*-alkyl derivatives and all previous hypotheses on intermediate additive products of alkyl iodides and $\text{CHAcNa}\cdot\text{CO}_2\text{Et}$ are unnecessary. The appearance of the ester in two forms is merely a secondary phenomenon. It is more reasonable to start from the ester itself and not from the ion; dissociation is then the primary process. The enol form shows the mesomeric phenomena

without eliminating $\bar{\text{H}}$ but the content of the mesomeric form, $\text{OH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, in the enol form is small. Since $\bar{\text{O}}\text{H}$ is strongly acidic and $\bar{\text{C}}\text{H}$ is strongly basic this mesomerism causes an enhanced acidity of the enolic form and simultaneously a strengthening of the basic character. Mesomerism occurs to such a small extent that the basic strength of CH is small. A direct conversion of the enol into the keto-form, which may be considered as an aceto-neutralisation of the enol form, does not occur with measurable rapidity since, generally, the neutralisation of weak bases is a slow process. Compounds with the group $\text{OH}\cdot\text{C}\cdot\text{N}^-$ differ from the enols because N can pass from the ter- to the quinque-valent state:

$\text{OH}\cdot\text{C}\cdot\text{N}^- \rightleftharpoons \bar{\text{O}}\cdot\text{C}\cdot\text{NH} \longleftrightarrow \text{O}:\text{C}\cdot\text{NH}^-$. When, as is usual, OH is distinctly acidic and N is distinctly basic the enol form readily passes to equilibrium in the zwitterion form (or, more correctly, the mesomeric system defined above), and the separate isolation of keto- and enolic forms is impossible. Examples are the tautomerism of amides and the lactam-lactim tautomerism (uric acid, isatin, hydroxypyridines), and, possibly, that of hydroxyazo-compounds. The mesomeric formulae $\text{R}\cdot\text{CO}\cdot\text{NH}_2 \rightleftharpoons \text{R}\cdot\text{C}(\bar{\text{O}})\cdot\text{NH}_2$ and $\text{R}\cdot\text{CS}\cdot\text{NH}_2 \rightleftharpoons \text{R}\cdot\text{C}(\bar{\text{S}})\cdot\text{NH}_2$ explain all the observations regarded hitherto as a consequence of tautomerism. The importance of the zwitterion formula for amides and thioamides is shown by their large dipole moments and from the observation that the C—N distance is smaller than that calc. The contribution of this formula to the structure is usually small and almost disappears in the *N*-alkyl derivatives. A tautomerism $\text{C}(\bar{\text{O}})\cdot\text{NH}_2$ to $\text{C}(\text{OH})\cdot\text{NH}$ is funda-

mentally possible but the enolisation is usually very small because of the greatly contrasted character of $\cdot\text{NH}$ and $\cdot\text{OH}$. Actually the spectroscopic identification of the enolic form of amide or thioamide (ultra-red or Raman spectrum) has never been recorded. The arguments can be extended to $\text{CO}(\text{NH}_2)_2$ and $\text{CS}(\text{NH}_2)_2$ but reasons are advanced for expecting tautomerism among uric acid derivatives. The possibility that tautomeric phenomena in general can be treated from the viewpoint of mesomerism is negated by the behaviour of the normal and *aci*-forms of $\text{CHR}_2\cdot\text{NO}_2$. The ions $\bar{\text{C}}\text{R}_2\cdot\text{NO}_2$ and $\text{CR}_2\cdot\text{NO}\bar{\text{O}}$ cannot be mesomeric since they have not the same spatial configuration and therefore differ from one another in the position of the at. nuclei as well as in electron distribution.

H. W.

Action of hydrogen cyanide on alkylideneacetoacetic esters. I. Preparation of α -substituted γ -ketonic acids. II. Preparation of butyrolactonedicarboxylic acids. HUAN (Bull. Soc. chim., 1938, [v], 5, 1341—1345, 1345—1350).—I. The double linkings only of compounds $\text{CHR}\cdot\text{C}(\text{Ac})\cdot\text{CO}_2\text{Et}$ (I) [$\text{R} = \text{Me}, \text{Pr}, \text{b.p. } 120\text{--}121^\circ/20 \text{ mm.}, \text{Ph}]$ are attacked by aq. $\text{EtOH}\text{--}\text{KCN}$ (not aq. KCN) at 0° to give $\text{CN}\cdot\text{CHR}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, converted by refluxing with aq. HCl (with or without AcOH) into α -methyl-, b.p. $138\text{--}141^\circ/11 \text{ mm.}$ [*Et* ester, b.p. $87^\circ/11 \text{ mm.}$ (*semicarbazone*, m.p. 120°)], α -propyl-, b.p. $162\text{--}163^\circ/15 \text{ mm.}$ [*semicarbazone*, m.p. 165° ; *Et* ester, b.p. $125\text{--}126^\circ/21 \text{ mm.}$, and its *semicarbazone*, m.p. 137°], and α -phenyl- [*semicarbazone*, m.p. $215^\circ, 245^\circ$ (decomp.), α rate of heating; *Et* ester, m.p. $41\text{--}42^\circ$, and its *semicarbazone*, m.p. $205^\circ, 212^\circ$ (decomp.) (*loc. cit.*)] γ -lactonic acids, with smaller amounts of the corresponding γ -lactones of α -methyl-, b.p. $90\text{--}92^\circ/14 \text{ mm.}$ and α -propyl-, b.p. $114\text{--}115^\circ/19 \text{ mm.}$, γ -hydroxy- Δ^8 -pentenoic acids (cf. Ruhemann, J.C.S., 1904, 85, 1454).

II. Compounds (I) ($\text{R} = \text{Me}, \text{Pr}, \text{Ph}$) and aq. $\text{HCN}\text{--}\text{KCN}\text{--}\text{EtOH}$, then aq. $\text{AcOH}\text{--}\text{EtOH}$ at 0° , followed by refluxing with HCl for 6 hr., afford γ -hydroxy- β - γ -dicarboxy- α -methyl-, m.p. 188° (*Et* ester, b.p. $183\text{--}184^\circ/22 \text{ mm.}$), α -propyl-, m.p. 190° (*Et* ester, b.p. $195\text{--}196^\circ/21 \text{ mm.}$), and α -phenyl-, m.p. 207° (217°) (*loc. cit.*) (*Et* ester, m.p. 69°), n -valerolactones, with small amounts of the corresponding γ -lactonic acids.

A. T. P.

Characterisation of carboxylic acids as ureides [acyldiarylcarbarnides] by means of carbodimides. III. F. ZETZSCHE and H. LINDLAR (Ber., 1938, 71, [B], 2095—2102; cf. A., 1938, II, 358).—Anhyd. and hydrated $\text{H}_2\text{C}_2\text{O}_4$ and carboditolyl- (I) or carbodibromophenyl- (II)-imide in Et_2O , alcohols, COMe_2 , dioxan, or $\text{C}_5\text{H}_5\text{N}$ give the corresponding diarylcarbarnide, CO, and CO_2 . With carbodi-*p*-dimethylaminophenylimide (III) *di-p*-dimethylaminophenylcarbarnide oxalate, m.p. 194° , is also formed. $\text{CH}_2(\text{CO}_2\text{H})_2$ and (I) in Et_2O , COMe_2 , COMeEt , or $\text{C}_5\text{H}_5\text{N}$ at room temp. or the b.p. yield dark-coloured resins and $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$. With (III) in Et_2O the products are $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ and the diureide, $\text{C}_3\text{H}_4\text{O}_4\text{N}_8$, m.p. 165° . Monomeric C_3O_2 is not detected. $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ and (I) give

$\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$ and $(\cdot\text{CH}_2\cdot\text{CO})_2\text{O}$ in Et_2O or COMe_2 . In absence of $\text{C}_5\text{H}_5\text{N}$ (III) behaves similarly whereas in its presence the *monoureide*, $\text{C}_{21}\text{H}_{26}\text{O}_4\text{N}_4$, m.p. 136° , is produced in 12% yield. In absence of $\text{C}_5\text{H}_5\text{N}$ glutaric acid resembles $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ in its action towards (I) and (III) whereas in presence thereof it affords the carbamide and *glutarditolylureide*, m.p. 239° , and *glutarmonodi-p-dimethylaminophenylureide*, m.p. 147° . In COMe_2 at room temp. or in boiling Et_2O adipic acid and (I) give the corresponding *monoureide* (IV), m.p. $154\cdot5^\circ$, and *diureide*, m.p. 247° (decomp.) after softening at 200° or m.p. 210° (decomp.) and, after re-solidification, m.p. 247° if placed in a bath preheated to 190° . With (III) in $\text{C}_5\text{H}_5\text{N}$ the *diureide*, $\text{C}_{40}\text{H}_{50}\text{O}_4\text{N}_8$, m.p. $233\text{--}234^\circ$, is obtained whereas in boiling Et_2O the *monoureide*, m.p. 174° , results. (IV) and (III) in COMe_2 at room temp. give *adip-p-ditolyl-p-dimethylaminophenyl-diureide*, m.p. $194\text{--}206^\circ$. Conc. or anhyd. HCO_2H and (I) or (III) give CO and *formyl-di-p-tolylcarbamide*, m.p. $145\text{--}146^\circ$, or *formyl-di-p-dimethylaminophenylcarbamide*, m.p. $154\cdot5^\circ$, respectively. H. W.

Reaction between potassium permanganate and oxalic acid, and decomposition of potassium mahnganioxalate.—See A., 1938, I, 635.

Exchange of oxygen atoms between water and organic compounds. M. KOZUMI and T. TITANI (Bull. Chem. Soc. Japan, 1938, 13, 607—617).—The exchange of ^{18}O from H_2^{18}O and certain substances at $100\text{--}130^\circ$ over varying periods (1—48 hr.) has been investigated. The no. of exchangeable O atoms in the following compounds is given in parentheses; glucose (1), PhCHO (1), BzOH (1), $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ (4), PhOH (0), maleic acid (4), fumaric acid (2), $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ (0), $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ (0).

J. D. R.

Condensation of sebacic acid with glycerol or pentaerythritol. G. S. PETROV, K. A. ANDRIANOV, and S. I. DSHENTSCHELSKAJA (Prom. Org. Chim., 1938, 5, 619—622).—Sebacic acid heated at 100° with glycerol (I) (12 hr.) or pentaerythritol (II) (3 hr.) yields gelatinous products, sol. in EtOH , COMe_2 , 1:1 $\text{EtOH}\text{-C}_6\text{H}_6$, or AcOH , but not in CCl_4 . The velocity of the reaction is greater with (II) than with (I), owing to the greater $\text{CH}_2\cdot\text{OH}$ group content of (II). The products quantitatively regenerate acid and alcohol when hydrolysed with 2·5N-KOH in EtOH , and are therefore esters, and not polymerisation products.

R. T.

Methyl tetronate, α -chloro-, α -bromo-, and α -iodo-tetronate. W. D. KÜMLER (J. Amer. Chem. Soc., 1938, 60, 2532).—*Me tetronate*, m.p. 63° , α -chloro-, m.p. 66° , α -bromo-, m.p. 116° , and α -iodo-tetronate, m.p. 158° , $\text{OMe}\cdot\text{C}\begin{smallmatrix} \text{CX}\cdot\text{CO} \\ \text{CH}_2\cdot\text{O} \end{smallmatrix}$, are obtained from the appropriate acid by CH_2N_2 .

R. S. C.

Reduction of aconitic acid at the dropping mercury cathode. H. SIEBERT (Z. Elektrochem., 1938, 44, 768—769).—Reduction of aconitic acid (I) at the dropping Hg cathode leads exclusively to tricarballic acid (II). This result is not in accord with the view that, under the influence of strong adsorptive forces, (I), maleic, and fumaric acids exist as free $\text{CH}\cdot\text{CO}_2\text{H}$ radicals (A., 1937, I, 245), as in such

case succinic acid (III) should also be a reduction product. Previous reports of the production of (III) are due to the reactions of (II) being mistaken for those of (III). J. W. S.

Action of sulphur trioxide-water mixtures on citric acid. A. QUARTAROLI and O. BELFIORI (Annali Chim. Appl., 1938, 28, 297—301).—Citric acid with cold $\text{H}_2\text{S}_2\text{O}_7$ gives high yields of aconitic acid (I). H_2SO_4 (94—100%) gives (slowly at low, and rapidly at high, temp.) $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ and CO_2 ; at concns. $<94\%$, H_2SO_4 (which, in this respect, behaves like HCl , HBr , etc.) gives (I), max. yield being with 60% H_2SO_4 . The mechanism of the reactions is discussed. F. O. H.

Rearrangement of *l*-gulonic into *l*-ascorbic acid. F. ELGER (Festschr. E. C. Barell, Basel, 1936, 229—237; Chem. Zentr., 1937, i, 2992).—*l*-Ascorbic acid is obtained in 91·5 and 82·7% yield, respectively, by rapid stirring of *Me l*-gulonate with NaHCO_3 in MeOH at $65^\circ/4$ hr. and of diisopropylidene-*l*-gulonic acid hydrate and EtOH-HCl in CHCl_3 at the b.p./55 hr. Anhyd. NaOAc can be used in place of NaHCO_3 . H. B.

Volumetric determination of ascorbic acid.—See A., 1938, III, 1027.

Stability of ascorbic acid in solution.—See A., 1938, III, 1026.

Polarimetric determination of calcium gluconate. I. VINTILESCO, C. N. IONESCO, and N. STANCIU (J. Pharm. Chim., 1938, [viii], 28, 283—293).—10 c.c. of Ca gluconate solution containing $<4\%$ of the salt, 0·5 c.c. of AcOH , and 4·5 c.c. of saturated aq. $(\text{NH}_4)_2\text{MoO}_4$, are mixed and the rotation is determined. The concn. of Ca gluconate is given by $p = 100\alpha/226\cdot67l$ (α = rotation; l = length of tube). The method is more sensitive than those previously described. P. G. M.

Esterification of isopropylidenepolyhydroxyacids. W. WENNER (Festschr. E. C. Barell, Basel, 1936, 296—309; Chem. Zentr., 1937, i, 2991).—Esters are obtained from K $\alpha\beta\gamma$ -diisopropylidenegulosonate or isopropylideneglycerate and, e.g., $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ in xylene at $\sim 100^\circ$, but not from EtBr , CH_2PhCl , $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$, or $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ (I). In presence of Cu powder, (I) and other $\beta\gamma$ -unsaturated halides, however, give 50% of the ester. The following are described: β -diethylaminoethyl (II), b.p. $164\text{--}167^\circ/0\cdot14$ mm., γ -dimethylamino- $\beta\beta$ -dimethylpropyl, b.p. $187\text{--}188^\circ/3$ mm., allyl (III), m.p. 95° [reduced (H_2 , Pd-C, COMe_2) to the *Pr*^a ester, m.p. $73\text{--}74^\circ$], isobutenyl, m.p. $69\text{--}70^\circ$, and *Me*, m.p. $44\text{--}45^\circ$ (from Na salt and Me_2SO_4 in xylene at $120\text{--}130^\circ$), diisopropylidene-*l*-gulonic acid; β -diethylaminoethyl, b.p. $142\text{--}143^\circ/12$ mm., and allyl, b.p. $100\text{--}102^\circ/10$ mm., isopropylideneglycerate. Dropwise addition of MeOH-HCl to (II) in Et_2O gives the β -diethylaminoethyl ester hydrochloride, m.p. 156° , of isopropylidene-*l*-gulonic acid [allyl ester (+ H_2O), m.p. 110° , formed with (III) when reaction with Na salt and (I) is carried out in H_2O].

H. B.

Action of antimonious anhydride and antimony sulphide on thiol acids. Y. VOLMAR and E. WEIL

(Compt. rend., 1938, **207**, 534—536).—Antimoniothioglycollic acid, $\text{Sb}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2)(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})$, m.p. 201—202° (cf. A., 1906, i, 396), and *antimoniothiolactic acid*, $\text{Sb}(\text{CHMe}\cdot\text{S}\cdot\text{CO}_2)(\text{CHMe}\cdot\text{S}\cdot\text{CO}_2\text{H})$, m.p. 192°, are formed by the action of the SH-acids on Sb_2O_3 or red Sb_2S_3 , the reactions being analogous to those with the corresponding OH-acids (A., 1938, II, 347). Salts of the SH-acids have been prepared.

A. J. E. W.

Oxidation of aldehydes by oxygen of the air. A. RIECHE (Angew. Chem., 1938, **51**, 707—709).—Atm. oxidation of aldehydes gives first peracids, which with unchanged aldehyde give compounds, $\text{RCO}\cdot\text{O}\cdot\text{CHR}\cdot\text{OH}$ (I). These rapidly decompose in presence of H_2O to give $2\text{RCO}_2\text{H}$ or, if the H_2O is removed, thus: $2(\text{I}) \rightarrow (\text{RCO})_2\text{O} + 2\text{RCO}_2\text{H} + \text{H}_2\text{O}$.

R. S. C.

Photolysis of aldehydes and ketones in paraffinoid solution.—See A., 1938, I, 632.

Stereochemistry of the phenylhydrazones. K. A. JENSEN and B. BAK (J. pr. Chem., 1938, [ii], 151, 167—176).—Dipole measurements show that α -nitroformaldehydephenylhydrazone (I), m.p. 74°, and the β - (II) -compound, m.p. 90°, have respectively the *syn*- and *anti*-configuration; for comparison the dipole moments of *o*- and *p*- $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ have been measured. The dielectric const. of a solution of (II) in C_6H_6 falls rapidly by reason of the transformation of (II) into (I). Of the three benzylformaldehydephenylhydrazones described in the literature only two appear to exist. Dipole measurements show that the α -, m.p. 111°, and the β -, m.p. 146°, -compounds are respectively the *syn*- and the *anti*-derivatives. The two isomeric acetaldehydephenylhydrazones have the same dipole moment within the limits of experimental error, so that a determination of configuration is impossible in these cases. The phenylhydrazones of COMe_2 and MeCHO have nearly the same vals. The benzaldehydephenylhydrazone of lower m.p. described in the literature does not appear to be an individual compound.

H. W.

Effect of glyceraldehyde on carbohydrate breakdown. H. LEHMANN and J. NEEDHAM (Enzymologia, 1938, **5**, 95—99; cf. A., 1937, III, 471; Adler *et al.*, *ibid.*, 431).—The breakdown of glycogen with production of hexose monophosphate is inhibited by fresh but not by old solutions of *dl*-glyceraldehyde. Since fresh solutions contain the dimeric and old solutions the monomeric form of the aldehyde an explanation of the difference is provided. Glucolysis is inhibited by the monomeric form.

W. McC.

Photochemical decomposition of methyl ethyl ketone by wave-lengths from 1850 to 2000 Å.—See A., 1938, I, 632.

Decomposition of di-*n*-propyl ketone in the vapour phase and in solution.—See A., 1938, I, 632.

Behaviour of acetylacetone on irradiation. A. P. VITORIA (Congr. int. Quím. pura apl., 1934, **9**, II, 334—341; Chem. Zentr., 1937, i, 566).—The absorption spectrum of gaseous CH_3Ac_2 is continuous at high but exhibits a broad band (max. 2600 Å.) at

low concn. The Hg arc induces polymerisation ($\lambda < 3030 \text{ Å.}$) and decomp. to yield CO; solutions in CCl_4 behave similarly.

A. H. C.

Polyazines. II. Reaction of hydrazine hydrate with acetylacetone, acetonilacetone, and benzil. B. G. ZIMMERMAN and H. L. LOCHTE (J. Amer. Chem. Soc., 1938, **60**, 2456—2458; cf. A., 1936, 1000).—Gray's 12-membered ring compound (J.C.S., 1901, **79**, 682) from $(\text{CH}_2\cdot\text{COMe})_2$ and N_2H_4 could not be obtained. In dil., aq. solution 3:6-dimethylpyridazine (platinichloride, +1 or $4\text{H}_2\text{O}$) and a polymeride, $\text{COMe}\cdot\text{CH}_2\cdot[\text{CH}_2\cdot\text{CMc}\cdot\text{N}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2]_{184}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}_2$, m.p. 276° (decomp.; sinters at 260°) [*picrate*, m.p. 170—176° (decomp.); *platinichloride*, m.p. 260—266° (decomp.); *hydrochloride*, m.p. 200—201° (decomp.)], are obtained. In C_6H_6 a good yield of the azine-hydrazone, m.p. 136—137° (*loc. cit.*, 132°), is obtained. $(\text{CPh}\cdot\text{N}\cdot\text{NH}_2)_2$ with Bz_2 , Ac_2 , or CH_3Ac_2 gives tars. $\text{COPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}_2$ and Ac_2 in hot EtOH give the *azine*, $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$, m.p. 85·8°, or, on longer heating, the *diazine*, $\text{C}_{32}\text{H}_{26}\text{N}_4\text{O}_2$, m.p. 238·3° (decomp.). CH_3Ac_2 and N_2H_4 give only 3:5-dimethylpyrazole. The compound, $(\text{CPh}\cdot\text{N})_2$ (Curtius, A., 1889, 393), could not be obtained. The mol. wt. of resinous polymerides of this series in C_6H_6 (cryoscopy) appears to increase with the concn. of the solution.

R. S. C.

Preparation of β -glucose. R. L. WHISTLER and B. F. BUCHANAN (J. Biol. Chem., 1938, **125**, 557—559).—An 85% solution of α -glucose was heated to 100° in a vac. oven and nucleated with pure β -glucose. A solid mass of anhyd. crystals resulted. Recrystallisation from aq. EtOH produced yields up to 70% of pure β -glucose.

T. F. D.

Methylation of sugars. B. C. HENDRICKS and R. E. RUNDLE (J. Amer. Chem. Soc., 1938, **60**, 2563—2564).—Tetramethyl- α -*d*-glucose, -mannose, and -galactose are best obtained by methylating first with $\text{Me}_2\text{SO}_4\text{--CCl}_4$ -conc. aq. NaOH and then with Na-MeI in liquid NH_3 .

R. S. C.

Methylation of α -methylglucoside by thallos hydroxide and methyl iodide. C. C. BARKER, E. L. HIRST, and J. K. N. JONES (J.C.S., 1938, 1695—1698).—The TI compound formed from α -methylglucoside and excess of TlOH , when treated with MeI and hydrolysed, yields tetramethylglucose, 2:4:6- (I), 2:3:6-, and in smaller quantities 2:3:4- and 3:4:6-trimethylglucose. The β -methylglucoside of (I) is oxidised (Br) to 2:4:6-trimethyl-8-gluconolactone, b.p. 150° (bath)/0·01 mm., $[\alpha]_D^{20} +104^\circ$ in CHCl_3 , $+87^\circ$ in $\text{H}_2\text{O} \rightarrow 37^\circ$ (const. val.), converted by NH_3 in Et_2O into 2:4:6-trimethylgluconamide, m.p. 98°, $[\alpha]_D^{21} +54^\circ$ in MeOH.

J. D. R.

Addition compounds of carbohydrates. IV. Potassium hydroxide compounds of the methylglucosides, maltose, amylose, and cellulose. W. J. HEDDLE and E. G. V. PERCIVAL (J.C.S., 1938, 1690—1695; cf. A., 1937, II, 52).— α - or β -Methylglucoside (or its tetra-acetate) with KOH in EtOH and Et_2O affords the compound, $\text{C}_7\text{H}_{14}\text{O}_6\cdot\text{KOH}$, which, when methylated (Me_2SO_4), acetylated,

hydrolysed, and treated with $\text{NHPh}\cdot\text{NH}_2$ yields 6-methylglucosazone. The KOH is therefore associated with the $\text{CH}_2\cdot\text{OH}$ groups. Similarly, maltose forms the compound, $\text{C}_{12}\text{H}_{22}\text{O}_{11}\cdot 3\text{KOH}$ (I), from which by methylation followed by acetylation a non-reducing syrup is obtained; this when hydrolysed and acetylated yields 2 : 6-dimethylglucose triacetate and 2-methylglucose tetra-acetate, indicating that the KOH in (I) is associated with the reducing group and with $\text{C}_{(2)}$ and $\text{C}_{(6)}$ in the non-reducing unit. Amylose yields the compound, $(\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{KOH})_x$, which when methylated and hydrolysed yields derivatives of 2-methylglucose (II). The cellulose derivative, $(\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{KOH})_x$, after methylation, hydrolysis, glucoside formation, and acetylation also yields derivatives of (II) and no 6-methylglucose derivatives. It is suggested that the $\text{CH}_2\cdot\text{OH}$ residues in cellulose are not available for complex formation, being involved in cross-linkings.

J. D. R.

Glycofuranosides and thioglycofuranosides.
IV. Direct formation of dimethyl acetal and preparation of α -ethylfuranoside from *l*-rhamnose ethyl mercaptal. J. W. GREEN and E. PACSU (J. Amer. Chem. Soc., 1938, **60**, 2288—2289; cf. A., 1938, II, 430).—*l*-Rhamnose Et mercaptal, HgCl_2 , HgO , and CaSO_4 in EtOH at 25° give a little α -ethyl-*l*-rhamnofuranoside, m.p. $54\text{--}56^\circ$, $[\alpha]_D^{20} -95.5^\circ$ in H_2O , and much syrup. In MeOH, however, 5% of *l*-rhamnose Me_2 acetal, m.p. $123\text{--}124^\circ$, $[\alpha]_D^{20} +10.2^\circ$ in H_2O , is obtained.

R. S. C.

Hydrolysis of 3-*p*-toluenesulphonyl derivatives of galactose. E. E. PERCIVAL and E. G. V. PERCIVAL (J.C.S., 1938, 1585—1587).—2 : 4 : 6-Trimethylmethylgalactoside (I) in $\text{C}_5\text{H}_5\text{N}$ with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ yields 2 : 4 : 6-trimethylmethylgalactoside 3-*p*-toluenesulphonate (II), m.p. $119\text{--}120^\circ$, $[\alpha]_D +84^\circ$ in CHCl_3 , which with $\text{HCl}\text{-Ac}_2\text{O}$ gives 1-chloro-2 : 4 : 6-trimethylgalactose 3-*p*-toluenesulphonate, m.p. 138° , $[\alpha]_D^{20}$ in $\text{CHCl}_3 +30^\circ \rightarrow +96^\circ$ in 96 hr. This, on hydrolysis (NaOMe), followed by methylation ($\text{MeI}\text{-Ag}_2\text{O}$) and hydrolysis, yields tetramethylgalactopyranose (identified as anilide), and no gulose derivatives, whence it is concluded that Walden inversion does not take place on removal of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2^-$. (II) is resistant to 24 hr. hydrolysis with NaOMe , but in 100 hr. yields (I), whilst with $\text{H}_2\text{SO}_4\text{-aq. EtOH}$ the material is unchanged in 50 hr.

J. D. R.

Ring structure of methylgalactofuranoside. W. N. HAWORTH, E. L. HIRST, D. I. JONES, and H. WOODWARD (J.C.S., 1938, 1575—1577).—Methyl-*d*-galactofuranoside (improved prep.) when methylated ($\text{Me}_2\text{SO}_4\text{-NaOH}$ and $\text{MeI}\text{-Ag}_2\text{O}$) yields tetramethylmethylgalactofuranoside (I), simultaneously hydrolysed and oxidised ($\text{HBr}\text{-Br}$) to a mixture of tetramethyl- δ - and - γ -galactonolactone (II), which with $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NH}_2$ yields 2 : 3 : 5 : 6-tetramethylgalactonic acid-*p*-bromophenylhydrazide, m.p. $134\text{--}136^\circ$, $[\alpha]_D^{17} +19.5^\circ$ in MeOH, from which pure (II) may be regenerated with HCl . Hydrolysis of (I) ($0.1\text{N}\text{-HCl}$) gives tetramethylgalactofuranose (III), which when heated yields octamethyldigalactofuranose, b.p. 193° (bath)/ 0.02 mm. , $[\alpha]_D^{19} -67^\circ$ in H_2O [hydrolysed to (III)], and when oxidised gives (II). Oxidation of

(II) with HNO_3 yields *d*-dimethoxysuccinic acid, proving its γ -structure.

J. D. R.

Ketoses. I. Structure of α -*l*-sorbitose. (MME.) Y. KHOUVINE and G. ARRAGON (Bull. Soc. chim., 1938, [v], 5, 1404—1415; cf. A., 1937, II, 485; 1938, II, 219).— α -*l*-Sorbitose (I), Ac_2O , and ZnCl_2 ($\text{C}_5\text{H}_5\text{N}$) at 0° for 4 hr. (3 hr.) give the Ac_4 derivative (II), m.p. 101.5° ($+\text{Et}_2\text{O}$, m.p. $65\text{--}66^\circ$), $[\alpha]_{578}^{20} -22.5^\circ$ in CHCl_3 , -9.2° in MeOH. (II) and $\text{Ac}_2\text{O}\text{-H}_2\text{SO}_4$ afford α -*l*-sorbitoside penta-acetate (III), m.p. $+97^\circ$, $[\alpha]_{578}^{20} -52.4^\circ$ in CHCl_3 , -59.7° in MeOH, and (II) and $\text{Ac}_2\text{O}\text{-ZnCl}_2$ at room temp., or (I) and $\text{Ac}_2\text{O}\text{-ZnCl}_2$ at 50° , give ketosorbitose penta-acetate (IV), m.p. 99° , $[\alpha]_{578}^{20} +2.8^\circ$ in CHCl_3 , -14.1° in MeOH, which is reduced catalytically (Raney Ni) to an alcohol acetylated to *d*-iditol hexa-acetate, $[\alpha]_{578}^{20} -25.4^\circ$ in CHCl_3 (cf. Bertrand, A., 1904, ii, 760; 1905, i, 21). (I) [or (II), (III), or (IV)] and $\text{MeOH}\text{-HCl}$ give α -*l*-methylsorbitoside (V), m.p. 118.5° , $[\alpha]_{578}^{20} -100.0^\circ$ in MeOH, -92.0° in H_2O , converted by $\text{Ac}_2\text{O}\text{-C}_5\text{H}_5\text{N}$ at 0° for 4 hr. into the Ac_4 derivative, m.p. 88° , $[\alpha]_{578}^{20} -51.8^\circ$ in CHCl_3 , -48.4° in MeOH, also obtained from (II) and $\text{MeI}\text{-Ag}_2\text{O}\text{-MeOH}$ at 40° for 4 hr. (cf. Whistler and Hixon, A., 1937, II, 485). (V) in $\text{H}_2\text{O}\text{-CCl}_4$ at 50° , then Na_2CO_3 and $\text{Me}_2\text{SO}_4\text{-Na}_2\text{CO}_3$ at $<60^\circ$, and finally at 80° , or $\text{MeOH}\text{-MeI}\text{-Ag}_2\text{O}$ at 40° for 6 hr., affords tetramethyl- α -*l*-methylsorbitoside (VI), b.p. $45^\circ/0.0001\text{ mm.}$, $[\alpha]_{578}^{20} -46.2^\circ$ in CHCl_3 , -31.5° in MeOH, hydrolysed by aq. HCl to tetramethyl- α -*l*-sorbitose (VII), b.p. $51^\circ/0.0001\text{ mm.}$, $[\alpha]_{578}^{20} -15.5^\circ$ in CHCl_3 , $+4.9^\circ$ in MeOH. (I) and (VII) and aq. $\text{Na}_2\text{CO}_3\text{-Me}_2\text{SO}_4$ at 60° give tetramethyl- β -*l*-methylsorbitoside (VIII), b.p. $48^\circ/0.0001\text{ mm.}$, $[\alpha]_{578}^{20} -21.8^\circ$ in CHCl_3 , -11.8° in MeOH, hydrolysed to tetramethyl- β -*l*-sorbitose (IX), b.p. $51^\circ/0.0001\text{ mm.}$, $[\alpha]_{578}^{20} -4.1^\circ$ in CHCl_3 , $+3.7^\circ$ in MeOH, which with $\text{HCl}\text{-MeOH}$ at 60° for $\frac{1}{2}$ hr. gives (VI). (VI), (VII), (VIII), or (IX) and HNO_3 (*d* 1.43—1.49) at 90° give Me_2 dimethoxysuccinate and Me_3 trimethoxyglutarate, converted by NH_2Me in MeOH into the di(methylamides), m.p. 205° and 167° , of *d*-dimethoxysuccinic and xylotrimethoxyglutaric acid, respectively. Raman spectra of (I), (VI), (VII), (VIII), and (IX) do not indicate C:O. (IV), unlike (II) and (III), gives a band at 2800 A. in the ultra-violet.

A. T. P.

Conversion of uronic acids into corresponding hexoses. VII. Catalytic reduction of methyl ester of hexamethylmethylglycoside of aldobionic acid (of gum arabic) to methylglycoside of hexamethyl-6-glucosidogalactose. Further methylation to methylglycoside of heptamethyl-6-glucosidogalactose. P. A. LEVENE, G. M. MEYER, and M. KUNA (J. Biol. Chem., 1938, **125**, 703—707).—Cryst. aldobionic acid hydrate was converted into Me hexamethylaldobionate, $\text{C}_{20}\text{H}_{36}\text{O}_{12}$, b.p. $220\text{--}240^\circ/2\text{ mm.}$, which was hydrogenated (Cu chromite) to $\text{C}_{19}\text{H}_{35}\text{O}_{11}$, m.p. $140\text{--}141^\circ$; this was re-methylated giving the methylglycoside of heptamethyl-6-glycosidogalactose, $\text{C}_{20}\text{H}_{38}\text{O}_{11}$, m.p. 73° , $[\alpha]_D^{25} -28.8^\circ$ in abs. EtOH.

T. F. D.

Preparation of α - and β -gentiobiose octaacetate. D. D. REYNOLDS and W. L. EVANS (J. Amer. Chem. Soc., 1938, **60**, 2559—2561).—Under anhyd. conditions (CaSO_4 etc.) β -*d*-glucose 1 : 2 : 3 : 4-

tetra-acetate yields 82% of β -gentiobiose octa-acetate. α -Gentiobiose octa-acetate is similarly obtained from syrupy α -D-glucose tetra-acetate. Prep. of the tetra-acetates is improved. R. S. C.

Preparation of quinol- β -glucoside from crude arbutin and the products of its reaction with diacetylorthonitric acid. B. REICHERT and W. TURKEWITSCH (Arch. Pharm., 1938, 276, 397—408).—Arbutin (I), new m.p. 199.5—200°, $[\alpha]_D^{20}$ -64.3° in H_2O , is separated from its accompanying Me ether by conversion in NaOH-MeOH- H_2O into the 2:4-dinitrophenyl ether (II), $+3H_2O$, m.p. 173°, and anhyd., m.p. 188.5—189° [Ac_4 derivative (III), m.p. 148—149°], and liberation therefrom by hot, aq. NaOH. With HNO_3 - Ac_2O at 0° (I) gives 2:6-dinitroarbutin 4-acetate (IV), $+H_2O$, m.p. 152°, hydrolysed by hot 10% H_2SO_4 to 2:6-dinitroquinol, m.p. (anhyd.) 137° or $(+xH_2O)$ 95—96° (Me ether, m.p. 112°), which is also obtained from p - C_6H_4 (OAc) $_2$ and HNO_3 - Ac_2O at 100°. With Ac_2O - C_5H_5N at 100° (IV) gives 2:6-dinitroarbutin tetra-acetate, m.p. 148—149° (free phenolic OH; Me ether, m.p. 101°), and with Ac_2O - H_2SO_4 the penta-acetate, m.p. 145°. Arbutin Me ether tetra-acetate and Ac_2O - HNO_3 at 100° give the 2- NO_2 -derivative, m.p. 162—163°, hydrolysed by 5% HCl-EtOH to 2:4:1- NO_2 - C_6H_3 (OMe)-OH. With HNO_3 - Ac_2O at room temp. (III) gives the 2- NO_2 -derivative, m.p. 173°, but 65% HNO_3 in a little AcOH gives 3:5:2':4'-tetranitro-4-hydroxydiphenyl ether, m.p. 195—196°, also obtained from (II) by warm HNO_3 - Ac_2O . R. S. C.

Electrodialyser for preparation of β -amylose. S. REDFERN (Cereal Chem., 1938, 15, 712—715).—Apparatus for the electrodialysis of starch is described. β -Amylose prepared by this means from maize and potato starches behaved almost identically towards malt amylase. E. A. F.

Polylævans formed by the carbohydrate metabolism of certain bacteria. S. VEIBEL (Biochem. J., 1938, 32, 1949—1952).—Gram-negative bacteria from milk, and certain soil bacteria (*Actinomycetes*), grown on a 2% sucrose-agar medium yield a non-reducing polysaccharide (Ac_3 derivative, m.p. 160—170°, $[\alpha]_D > +11^\circ$ in $CHCl_3$; Me_3 derivative, m.p. 140° after softening at 122°, $[\alpha]_D -57^\circ$ to -60° in $CHCl_3$) hydrolysed (HCl) to fructose. J. D. R.

Oxidation of starch. Action of bromine on gelatinised corn starch. G. FELTON, F. F. FARLEY, and R. M. HIXON (Cereal Chem., 1938, 15, 678—689).—Oxidation of starch by Br occurs in the four ways theoretically expected. Oxidation of primary OH groups to uronic acids is a max. at 6 equivs. of Br per glucose unit; non-uronic CO_2H groups are produced when >3 equivs. of Br are present. *sec.* OH groups are oxidised to $\cdot CO\cdot$, with a max. at two Br equivs., and glycol groups are oxidised with rupture of the pyranose ring. β -Amylose reacts in the same way as α -amylose, but in $\frac{1}{2}$ of the time. E. A. F.

Starch. (A) Lintner's isomaltose and " β -glucosidomaltose." A. R. LING. (B) A polyamylose, Baker's α -amylodextrin. A. R. LING, W. A. CARTER, and R. S. POTTER. (C) A poly-

hexosan ("stable dextrin" of H. T. Brown). A. R. LING and W. A. CARTER (J. Inst. Brew., 1938, 44, 419—421, 422—423, 424).—(A) The isomaltose of Lintner and of Ling and Nanji consists of a mixture of maltose and a non-reducing dihexosan, the latter being convertible completely into maltose by diastatic action. Emulsin is without action on the "isomaltose" mixture. Re-examination of samples of β -glucosidomaltose proves these also to be mixtures which are inappreciably affected by emulsin but yield glucose with maltase.

(B) A method for the prep. of polyamylose is described. This substance is related to amylopectin, and is better described as polyamylose than as a dextrin; the available evidence does not support the further alternative name of $\alpha\beta$ -hexa-amylose. $MgSO_4$ -pptd. diastase converts this polyamylose into maltose, another sugar which is probably a trisaccharide, and a trihexosan, together with a little glucose.

(C) Starch converted into the "stable dextrin" stage yielded maltose and an EtOH-insol. residue. The latter, mixed with purified kieselguhr, dried, and extracted with MeOH, gave further maltose as sol. sugar and an insol. non-reducing polyhexosan residue, $[\alpha]_D^{200}$, mol. wt. 1306, polymerisation having apparently taken place. The polyhexosan with diastase yields maltose and, apparently, dihexosan. I. A. P.

Mol. wts. of cellulose and cellulose derivatives.

—See A., 1938, I, 618.

Proteinogenic alkyl alcamines. II. C. C. CHRISTMAN and P. A. LEVENE (J. Biol. Chem., 1938, 125, 709—714).—Reduction of esters of NH_2 -acids by H_2 in the presence of Cu chromite produces *N*-disubstituted alkamines from solution in MeOH or EtOH but the *N*-monosubstituted derivatives from reduction in solution in the higher normal alcohols. *N*-Diethyl-dl-leucinol (picrate, m.p. 79—80°), *N*-dimethyl-dl-phenylalaninol, *N*-mono-*n*-propyl-dl-leucinol, m.p. 52—53°, *N*-di-*n*-propyl-dl-leucinol hydrochloride, m.p. 130—131°, *N*-monoisopropyl-dl-leucinol hydrochloride, m.p. 92—93°, *N*-mono-*n*-butyl-dl-leucinol hydrochloride, m.p. 148—149°, and *N*-monoisobutyl-dl-leucinol hydrochloride, m.p. 151—152°, have thus been prepared by catalytic reduction in the appropriate alcohol. T. F. D.

Ethylenediamine and propylenediamine vanadates. E. H. HUFFMAN (J. Amer. Chem. Soc., 1938, 60, 2227—2228).— $2(CH_2\cdot NH_2)_2\cdot H_4V_6O_{17}\cdot 4H_2O$ and $2C_3H_6(NH_2)_2\cdot H_4V_6O_{17}\cdot 2H_2O$ are prepared by adding V_2O_5 to the requisite diamine in H_2O and then slowly adding H_2O_2 , keeping the temp. below 60°. Three methods of prep. of $(CH_2\cdot NH_2)_2\cdot 2HVO_3$ are given. The compounds are insol. in EtOH, Et_2O , $COMe_2$, dioxan, and C_6H_6 , almost insol. in H_2O , and sol. in aq. NH_3 , $(CH_2\cdot NH_2)_2$, $C_3H_6(NH_2)_2$, and 30% H_2O_2 . E. S. H.

Chemical nature and nomenclature of choline derivatives. A. DEM. WELCH (Science, 1938, 88, 333—334).—The unsuitability of the names "choline," "choline hydrochloride," and "betaine aldehyde" is discussed. L. S. T.

Amino-derivatives of pentaerythritol. I. Preparation. A. LITHERLAND and F. G. MANN (J.C.S.,

1938, 1588—1595).—Interaction of $C(CH_2Br)_4$ and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NHNa}$ yields *tetrakis-p-toluenesulphonamidomethane* (I), m.p. 248°, and *N-p-toluenesulphonyl-3:3-bis-p-toluenesulphonamidomethyltrimethyleneimine* (II), m.p. 214°. Hydrolysis of (I) with 80% H_2SO_4 yields *tetrakisaminomethylmethane* (III) [disulphate, (IV), m.p. 303°; *tetrapicrate trihydrate*, m.p. 196—197° (decomp.); *tetrahydrochloride*, decomp. >260°, formed from (I) and HCl , which at 265—270° yields NH_4Cl ; Bz_4 derivative, m.p. 276°]. (III) with $\text{Me}_2\text{SO}_4\text{--NaOH}$ yields *tetrakisdimethylaminomethane* (V) (*tetrahydrochloride trihydrate*, m.p. 231°; *tetrapicrate*). With MeI in MeOH (V) yields a *dimethiodide*, which at 150—155° gives the *tetramethiodide (dihydrate)*. The Na derivative of (II) with CH_2PhBr at 170° yields *N-p-toluenesulphonyl-3:3-bis-p-toluenesulphonbenzylamidomethyltrimethyleneimine*, m.p. 181°. Hydrolysis of (II) by 70% H_2SO_4 affords *hydroxymethyltrisaminomethylmethane* [tripicrate (+3 H_2O), m.p. 145° (decomp.); *trihydrochloride* (VI), m.p. 298° (decomp.); *triplatinichloride* (+2 H_2O); Bz_3 derivative, m.p. 231—232°; *tri-o-nitrobenzoyl* derivative, m.p. 229°]. Hydrolysis of (II) with HCl at 160—170° gives *chloromethyl-* (VII), m.p. 271—272° (decomp.), and with HBr , *bromomethyl-tris-p-toluenesulphonamidomethylmethane*, m.p. 268°. Rapid heating of (II) with HCl to 200° yields *chloromethyltrisaminomethylmethane trihydrochloride* (VIII), m.p. 276° (decomp.) (*tripicrate*, m.p. 122°), also formed in the same way from (VII). Steam-distillation of (VIII) with NaOH at 140° yields *3:3-bisaminomethyltrimethyleneimine* [*trihydrochloride*, m.p. 272° (decomp.); *tripicrate* (+2 H_2O), m.p. 212—213° (decomp.; loses H_2O at 140°); *tri-o-nitrobenzoyl* derivative, m.p. 285°, hydrolysed by HCl to (VI)]. *Trisbromomethylacetoxymethylmethane* with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\cdot\text{NHNa}$ at 180° yields *1-p-toluenesulphonamido-2:2-bis-p-toluenesulphonamidomethylecyclopropane* (IX), m.p. 171° (the Na_3 derivative of which with CH_2PhBr yields a *tribenzyl* derivative, m.p. 146°), and $\text{NN'-di-p-toluenesulphonylbis(trimethyleneimine-3:3'-spiran)}$, m.p. 186°, hydrolysed by HCl at 140° to *bis(trimethyleneimine-3:3'-spiran)* (X) [*dipicrate*, m.p. 243° (decomp.); *dihydrochloride*, m.p. 275° (decomp.); *di-o-nitrobenzoyl* derivative, m.p. 218° (hydrolysed by HCl to an amine, probably *bishydroxymethylbisaminomethylmethane*)]. Hydrolysis of (IX) (HCl at 140°) yields (X). J. D. R.

Formation of benzene derivatives from dimethylaminobutanone and malonic or acetoacetic ester. C. MANNICH and J. P. FOURNEAU (Ber., 1938, 71, [B], 2090—2092).—At room temp. a mixture of $\text{NMe}_2\cdot[\text{CH}_2]_2\cdot\text{Ac}$, $\text{CH}_2(\text{CO}_2\text{Et})_2$, and NaOEt affords $\text{Et}_2\gamma$ -ketobutylmalonate, m.p. 154—158°/10 mm. (*semicarbazone*, m.p. 118°), in satisfactory yield. It is converted by boiling 10% H_2SO_4 into δ -keto-n-hexoic acid and by NaOEt into dihydroresorcinol. $\text{NMe}_2\cdot[\text{CH}_2]_2\cdot\text{Ac}$, $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, and NaOEt afford NHMe_2 and Et 4-keto-2-methyl- Δ^2 -cyclohexenecarboxylate (*semicarbazone*, m.p. 169°), hydrolysed to 1-methyl- Δ^1 -cyclohexen-3-one. H. W.

Amino-sugars. I. A case of acyl migration. T. WHITE (J.C.S., 1938, 1498—1500).—Salicylidene-glucosamine in $\text{C}_5\text{H}_5\text{N}$ with Ac_2O yields *acetoxymethyl-*

ideneaminoglucose 1:3:4:6-tetra-acetate, m.p. 132°, which with HCl in COMe_2 or AcCl in CHCl_3 gives *glucosamine 1:3:4:6-tetra-acetate hydrochloride*, decomp. 230°, converted by $\text{MeOH}\text{--NH}_3$ into *N-acetylglucosamine*. J. D. R.

Deuterium as indicator in the study of intermediary metabolism. XIII. Stability of hydrogen in amino-acids. D. RITTENBERG, A. S. KESTON, R. SCHOENHEIMER, and G. L. FOSTER (J. Biol. Chem., 1938, 125, 1—12).—Deutero-alanine and -leucine, the $\beta\gamma$ -dideutero-derivatives of *dl*-leucine and *dl*-valine, and $\beta\beta\gamma\gamma$ -tetra-deutero-homocystine lose no D when boiled with 20% HCl . $\beta\gamma$ -Dideuteromethionine loses approx. 6% of its D, probably because of slight decomp. when thus treated. Lysine takes up no D, proline and phenylalanine take up traces, and glycine, tyrosine, cystine, and glutamic acid take up less than 1 atom of D per mol., when boiled with 20% HCl or H_2SO_4 in dil. D_2O . The uptake of D is reversible. The D which enters tyrosine occupies the *o*-positions to the OH and is removed by treatment with aq. Br. Probably the entrance of D into cystine is due to racemisation and the entrance into glycine to production of pyrrolidonecarboxylic acid. Since H combined with C in NH_2 -acids is stable, D may be used as indicator in studying the metabolism of the acids. (Cf. A., 1938, III, 1032.)

Compounds related to canaline and canavaine. E. BOREK and H. T. CLARKE (J. Biol. Chem., 1938, 125, 479—494).—*N*-Benzoylcarboxymethoxylamine, m.p. 123°, isopropylidene- β -bromoethoxime, b.p. 36—45°/1 mm., isopropylidene- $\gamma\gamma$ -dicarbethoxypropoxime, b.p. 120—128°/2 mm., isopropylidenedicarbonypropoxime, m.p. 113°, $\gamma\gamma$ -dicarbethoxypropoxylamine hydrochloride, m.p. 103°, benzoyl- $\gamma\gamma$ -dicarbonypropoxylamine, m.p. 150°, benzoyl- γ -carboxypropoxylamine, m.p. 112°, γ -carboxypropoxylamine hydrochloride, m.p. 142°, methoxyguanidine sulphate, m.p. 145—146°, carboxymethoxyguanidine, m.p. 195°, γ -carboxypropoxylguanidine, m.p. 205°, and benzoyl- γ -bromo- γ -carboxypropoxylamine, m.p. 149°, were prepared and their titration curves determined. The apparent dissociation consts. of the carboxylated ethers of NH_2OH and hydroxyguanidine agree well with those of the corresponding groups in canaline and canavaine. T. F. D.

Trialkyl trithio-phosphorus, -antimony, and -bismuth compounds. A. LIPPERT and E. E. REID (J. Amer. Chem. Soc., 1938, 60, 2370—2371).— RSH and PCl_3 , best in NPhMe_2 at 70°, give Et_3 (I), b.p. 140—143°/18 mm., m.p. -32° to -31° (*methiodide*, m.p. 191°; HgBr_2 , m.p. 184°, HgI_2 , m.p. 187°, and AuCl_3 , m.p. 225°, *additive compounds*), Pr_3 , b.p. 164—169°/15 mm., m.p. -65° to -64° (*methiodide*, m.p. 191°; HgBr_2 , m.p. 176°, HgI_2 , m.p. 182°, and AuCl_3 , m.p. 208°, *additive compounds*), and Bu_3 trithiophosphite, b.p. 174—180°/15 mm., m.p. -101° to -100° (*methiodide*, m.p. 198°; HgBr_2 , m.p. 148°, HgI_2 , m.p. 162°, and AuCl_3 , m.p. 182°, *additive compounds*). Other unstable additive compounds are also formed by the products. These esters are stable to H_2O and acids, but are readily hydrolysed by alkali, and with Cl_2 or Br give R_2S_2 and H_3PO_4 ; however, (I) absorbs 2 I to give a product, which with H_2O

slowly yields hydrated crystals. With 3% H_2O_2 in AcOH (I) gives $\text{PO}(\text{SEt})_3$, b.p. 165–168°/15 mm., m.p. –24° to –23°, but stronger oxidising agents (60% H_2O_2 , HNO_3 , KMnO_4 , or Na_2CrO_4) give H_3PO_4 and RSO_3H . SbCl_3 and EtSH in NPhMe_2 give 30% of $\text{Et}_3\text{trithioantimonite}$, unstable, b.p. 167–170°/4 mm. (unstable iodide), but an 80% yield is obtained from NaSEt . $\text{Bi}(\text{NO}_3)_3$ and EtSH give Et_3BiS_3 , m.p. 200° (decomp.). R. S. C.

Preparation of glucose-1-phosphoric acid. W. KIESSLING (Biochem. Z., 1938, 298, 421–430).—At 100° 0.2N- NaOH hydrolyses hexose-di- and -6-phosphoric acid to the extent of 100 and 60%, respectively, in 3 min. but does not affect glucose-1-phosphoric acid (I). The prep. of pure cryst. K_2 glucose 1-phosphate, $\text{C}_6\text{H}_{11}\text{O}_9\text{PK}_2 + 2\text{H}_2\text{O}$, $[\alpha]_{\text{D}}^{20}$ (anhyd.) +106.78° (free acid, $[\alpha]_{\text{D}}^{20}$ +120°), from glycogen and rabbit muscle extract obtained by extraction with 1% aq. NaH_2PO_4 is described. Production of Embden's ester is prevented by maintaining high PO_4 concn. and oxidation-reduction by adding $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$. No dialysis is necessary. (I) is completely converted into glucose and H_3PO_4 by heating for 10 min. at 100° with $\text{N}\cdot\text{HCl}$. Long-dialysed muscle extract converts it irreversibly into an equilibrium mixture of glucose- (80–85%) and fructose-6-phosphoric acid with (probably) some mannose-6-phosphoric acid. This conversion is accelerated by Mg^{++} ; no other co-enzyme is required and NaF , phloridzin, insulin, and $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ have no effect. If $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ is added there is no accompanying production of glycerophosphate, and almost no production of hexose diphosphate. In the phosphorylation of glycogen it is not certain that adenylyl pyrophosphate has no power to act as a co-enzyme. As second co-enzyme Mg^{++} is replaceable by Mn^{++} , which is somewhat more active. W. McC.

Organo-silicon synthesis. I. Wurtz reaction with silicon chlorides. W. C. SCHUMB, J. ACKERMAN, jun., and C. M. SAFFER, jun. (J. Amer. Chem. Soc., 1938, 60, 2486–2488).—By applying the Wurtz reaction to SiCl_4 with EtBr , n -amyl chloride, PhCl , and $p\text{-C}_6\text{H}_4\text{PhCl}$, the products are SiEt_4 , $\text{Si}(n\text{-C}_5\text{H}_{11})_4$, b.p. 318°, SiPh_4 , and $\text{Si}(\text{C}_6\text{H}_4\text{Ph})_4$, m.p. 274°, respectively. Compounds SiR_4 are also obtained when the reaction is applied to Si_2OCl_6 with EtBr or PhCl . No evidence of the formation of hexa-substituted disilanes was obtained, the Si-Si or Si-O-Si linkings being invariably broken. E. S. H.

Reducing action of primary Grignard reagents. F. C. WHITMORE, A. H. POPKIN, J. S. WHITAKER, K. F. MATTIL, and J. D. ZECH (J. Amer. Chem. Soc., 1938, 60, 2458–2462).—With Bu^*COCl MgBu^*Br gives 27% of $\text{CH}_2\text{Bu}^*\text{Cl}$ and 69% of $\text{CHBu}^*\text{Bu}^*\text{OH}$, whereas MgBu^*Br gives 95% of $\text{CH}_2\text{Bu}^*\text{Cl}$ and only 1% of CHCu^*OH . An excess of MgBu^*Br with (*a*) AcCl , (*b*) EtOAc , (*c*) MeCHO , and (*d*) COMeBu gives, besides the usual products, (*a*) EtOH 8 and $\text{CHMeBu}\cdot\text{OH}$ 13, (*b*) $\text{CHMeBu}\cdot\text{OH}$ 3, (*c*) EtOH 18, and (*d*) $\text{CHMeBu}\cdot\text{OH}$ 9%, respectively. $\text{COMe}\cdot\text{CH}_2\text{Bu}^*$ with MgEtBr gives (?) a trace of $\text{CH}_2\text{Bu}^*\text{CHMe}\cdot\text{OH}$, of which 5.5% is obtained with MgPr^*Br , 5.7% with MgBu^*Br , and 3.4% with n -

$\text{C}_5\text{H}_{11}\cdot\text{MgBr}$. MgBu^*Br and $\text{Bu}^*\text{CO}_2\text{Et}$ give 40% of $\text{CHBu}^*\text{Bu}^*\text{OH}$, but not $\text{CH}_2\text{Bu}^*\text{OH}$, whereas MgBu^*Cl does not react in Et_2O , although possibly at higher temp. R. S. C.

Addition products of 3:4-dehydrocyclo tetramethylenesulphone.—See B., 1938, 1268.

Action of primary Grignard reagents on *tert.*-butylacetyl chloride. F. C. WHITMORE, A. H. POPKIN, J. S. WHITAKER, K. F. MATTIL, and J. D. ZECH (J. Amer. Chem. Soc., 1938, 60, 2462–2464).—The nature of R in $\text{CRR}'\text{R}''\text{COCl}$ may have a predominating effect on the amount of reduction occurring during reaction with MgAlkHal . $\text{CH}_2\text{Bu}^*\text{OH}$ and MgRBr ($\text{R} = \text{Et}$, Pr^* , Bu^* , or $n\text{-C}_5\text{H}_{11}$) give no $\text{CH}_2\text{Bu}^*\text{OH}$, but $\text{CH}_2\text{Bu}^*\text{CHR}\cdot\text{OH}$ was produced in 0, 24.4, 20.5, and 19.3% yield, respectively; the *tert.* carbinols, $\text{CH}_2\text{Bu}^*\text{CR}_2\cdot\text{OH}$, produced were dehydrated, when kept if $\text{R} = \text{Et}$, partly when distilled if $\text{R} = \text{Pr}^*$, and completely when distilled if $\text{R} = \text{Bu}^*$ or C_5H_{11} . $\text{CH}_2\text{Bu}^*\text{CO}\cdot\text{NH}_2$ gives by the Grignard reaction good yields of $\text{COR}\cdot\text{CH}_2\text{Bu}^*$, which with $\text{Al}(\text{OPr}^*)_3\text{-Pr}^*\text{OH}$ give $\beta\beta$ -dimethyl-*n*-heptan-, b.p. 85°/29 mm. (*phenylurethane*, m.p. 82°), -octan-, b.p. 95°/24 mm. (α -*naphthylurethane*, m.p. 70–70.5°), and -nonan-*ol*, b.p. 96°/13 mm. (*phenyl*-, m.p. 60.5–61°, and α -*naphthylurethane*, m.p. 63–63.5°), in 92, 93, and 89% yield, respectively. R. S. C.

Condensation of halogenobenzenes with unsaturated hydrocarbons and their halogen derivatives in presence of concentrated sulphuric acid. R. TRUFFAULT (Compt. rend., 1938, 207, 676–678).—Interaction of PhCl and PhBr with cyclohexene as described previously (A., 1936, 832) affords *p*-cyclohexyl-chloro-, b.p. 134°/16 mm.; and -bromo-benzene, b.p. 146°/16 mm., converted into *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ and *p*-cyclohexylbenzoic acid, respectively. PhCl and PhBr with $\text{CH}_2\text{CH}\cdot\text{CH}_2\text{Cl}$ afford α -chloro- β -*p*-chloro-, b.p. 117°/16 mm., and α -chloro- β -*p*-bromo-phenylpropane, b.p. 134–135°/15 mm., respectively. J. L. D.

The iodosous cation as an agent for aromatic substitution. I. MASSON and W. E. HANBY (J.C.S., 1938, 1699–1701; cf. A., 1937, II, 490).— I , I_2O_5 , and 90% H_2SO_4 give $\text{I}_2\text{O}_3\cdot\text{SO}_3$, which with PhNO_2 (in H_2SO_4) affords *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OI}$ (I) ($? + \text{H}_2\text{O}$), this being the first case of substitution by IO ; $m\text{-C}_6\text{H}_4\text{I}\cdot\text{NO}_2$ and iodonium salts, mainly with radical $(\text{C}_6\text{H}_3\text{I}\cdot\text{NO}_2)(\text{C}_6\text{H}_4\cdot\text{NO}_2)\text{I}^+$, are also formed, due to a secondary slow decomp. of (I) by H_2SO_4 (cf. Hartmann and Meyer, A., 1894, i, 242). (I) and $\text{Ac}_2\text{O}\cdot\text{AcOH}$ give the iodoso-diacetate, m.p. 143–147° (decomp.). Mechanisms of the reactions, involving ionic exchanges, are discussed. PhSP_3H and BzOH give IO -compounds, but the latter reaction is complicated. A. T. P.

Coloured by-product in the preparation of 1:3:5-triphenylbenzene from acetophenone. R. J. W. LE FÈVRE (J.C.S., 1938, 1467).—Autocondensation of COPhMe ($\text{K}_2\text{S}_2\text{O}_7\text{-H}_2\text{SO}_4$) at $\sim 150^\circ$ (cf. Odell and Hines, A., 1913, i, 172) gives a poor yield of *s*- $\text{C}_6\text{H}_3\text{Ph}_3$ (70% yield at 45°), and a pyrylium salt (I), converted by $\text{FeCl}_3\text{-HCl}$ into 2:4:6-triphenylpyrylium ferrichloride (5% yield), m.p. $\sim 273^\circ$ —

275°, identical with that prepared from CPhMe, PhCHO, FeCl₃, and Ac₂O (Dilthey, A., 1916, i, 829). The perchlorate, m.p. 288° (cf. A., 1933, 163), is obtained through the pyranol. Formation of (I) is probably through Bz₂O (cf. A., 1933, 1166).

A. T. P.

Induced oxidation of iodobenzene during the oxidation of acetaldehyde in an atmosphere of oxygen. W. P. JORISSEN and A. C. B. DEKKING (Rec. trav. chim., 1938, 57, 1125—1126).—When a solution of PhI in MeCHO is exposed to O₂, PhIO₂ is formed.

F. J. G.

Addition and additive products of halogens and benzene derivatives. XI. Action of chlorine on benzotrichloride, benzylidene chloride, benzyl chloride, and toluene. T. VAN DER LINDEN (Rec. trav. chim., 1938, 57, 1075—1086).—CPhCl₃ (I), saturated with Cl₂ in sunlight, yields in 8 months 1:2:3:4:5:6-hexachloro-1-trichloromethylcyclohexane (II), m.p. 102° [also obtained from (I) and liquid Cl₂ in a sealed tube], hydrolysed (H₂SO₄-SO₂) to γ -benzoic acid hexachloride. Hydrolysis of (II) with NaOH in EtOH or EtOAc yields at room temp. mixed isomerides of C₆H₂Cl₃·CCl₃, and at higher temp., mixed C₆H₃Cl₂·CO₂H and C₆H₂Cl₃·CO₂H. CHPhCl₂ with liquid Cl₂ yields rapidly 1:2:3:4:5:6-hexachloro-1-dichloromethylcyclohexane (III), m.p. 153°, hydrolysed (NaOH-EtOH or NaOH-EtOAc) to C₆H₃Cl₃·CHCl₂. Chlorination of CH₂PhCl in sunlight yields (III) whilst repeated chlorination of PhMe in sunlight yields (III) and 1:2:3:4:5:6-hexachloro-1-chloromethylcyclohexane, m.p. 267—269°, CPhCl₃, and *p*-C₆H₄Cl·CCl₃.

J. D. R.

Nuclear-substituted bromo-derivatives of isopropylbenzene. W. QVIST (Acta Acad. Aboensis math. phys., 1936, 10, No. 5, 39 pp.; Chem. Zentr., 1936, ii, 4005).—PhBr^{*s*} is brominated in presence of I and Fe under various conditions and the products are identified by oxidation of Pr^{*s*} to CO₂H and by prep. of derivatives. The following changes are established: PhPr^{*s*} → *p*-C₆H₄BrPr^{*s*} → 2:4- and 3:4-C₆H₃Br₂Pr^{*s*} → 2:4:5-C₆H₂Br₃Pr^{*s*} (I) → 2:3:4:5-C₆HBr₄Pr^{*s*} (II); side reactions are (I) → C₆HBr₅ and (II) → C₆Br₆. C₆H₅Pr^{*s*} was not found but C₆Br₅Me is a by-product in the further bromination of (I). The non-formation of derivatives containing two Br both *o*- to Pr^{*s*} is ascribed to steric hindrance. Differences in bromination and chlorination (cf. A., 1936, 1100) are noted.

Oxidation [HNO₃ (*d* 1.2) at 100°] of C₆H₃Br₂Pr^{*s*} gives 2:4-, m.p. 169—170°, and 3:4-dibromobenzoic acid, m.p. 235—236° [chloride, m.p. 66—67°; amide, m.p. 154—154.5°; 2:6-(NO₂)₂-derivative, m.p. 227.5—228.5°, by oxidation of (III) (below)]; HNO₃ (*d* 1.52) at 100° affords 3:4-dibromo-2:6-dinitrocumene (III), m.p. 132.5—133.5°, and 4:6-dibromo-1:3-dinitrobenzene, m.p. 117—117.5°. The last with EtOH-NH₂Ph at 100° and EtOH-NH₃ at room temp. or 120° affords respectively 1:3-dinitro-4:6-dianilinobenzene, m.p. 187.5—188°, and a bromodinitroaniline, m.p. 177—178°, or dinitrodiaminobenzene, m.p. >300°. 4-Bromo-2:6-dinitro-3-anilino-cumene, m.p. 133.5—134.5°, is obtained from (III) and EtOH-NH₂Ph. 2:4:5-C₆H₂Br₃Pr^{*s*} and HNO₃

(*d* 1.52) give 2:4:5-tribromo-3-nitrocumene (IV), m.p. 97.5—98.5°, and 2:4:5:1-C₆H₂Br₃·NO₂, m.p. 95—95.5° (with EtOH-NH₃ gives 4:5-dibromo-2-nitroaniline, m.p. 206.5—207.5°). 2:4:5-Tribromo-1:3-dinitrobenzene, m.p. 138—138.5° [from (IV), HNO₃ (*d* 1.52), and conc. H₂SO₄ at 100°], and EtOH-NH₂Ph afford 6-bromo-2:4-dinitro-1:3-dianilinobenzene, m.p. 197.5—198.5°. 2:4:5-Tribromobenzoic acid and its 3-NO₂-derivative have m.p. 203—204° and 249—250°, respectively. 6-Bromo-2:4-dinitro-1:3:5-trianilinobenzene, m.p. 173—174°, is prepared from NH₂Ph and the (NO₂)₂-derivative, m.p. 232.5—233.5°, of 1:2:3:5-C₆H₂Br₄, m.p. 99—100°. 2:3:4:5-Tetrabromocumene (NO₂-derivative, m.p. 73—74°) has m.p. 62.5—63.5°. H. B.

Hypiodous cations and their action on an organic reagent.—See A., 1938, I, 611.

Condensation of arylhalogenomethanes. S. C. OLIVIER and J. WIT (Rec. trav. chim., 1938, 57, 1117—1124).—The decomp. of 2-C₁₀H₇·CH₂Br (cf. A., 1938, II, 90) under the influence of the flask wall is traced to the catalytic influence of Fe₂O₃ in the glass. The decomp. follows the course $n\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Br} \rightarrow (\text{C}_{11}\text{H}_8)_n + n\text{HBr}$, and is facilitated by small quantities of Fe₂O₃ or Cu.

J. D. R.

Mobility of groups in 4-chloro-2-nitrodiphenyl sulphones. J. D. LOUDON and N. SHULMAN (J.C.S., 1938, 1618—1621; cf. A., 1937, II, 141).—Reactivity of compounds 2:4:1-NO₂·C₆H₃Cl·SO₂R (I) is much more sensitive to changes in attacking reagent than to alteration of R. (I) [R = NH₂, NC₅H₁₀, Me, Ph, *p*-C₆H₄Me, 2:5-C₆H₃Cl₂] and *p*-C₆H₄Me·SNa-NaOH-EtOH give rapid replacement of SO₂R to yield 4-chloro-2-nitro-*p*-tolyl sulphide (II), but excess of piperidine on the same derivatives gives a mixture of the three derivatives corresponding with replacement of each of the three substituents in (I) by NC₅H₁₀. Thus, (I) (R = Me), new m.p. 155—156°, heated in excess of piperidine for 5 min. (general method) affords 2-nitro-4-, m.p. 126° (that in greatest amount named first), and 4-chloro-2-, m.p. 134°, -piperidinophenylmethylsulphone, and 4-chloro-2-nitro-1-piperidinobenzene (III) (always in smallest amount). 2:5:1-C₆H₃Cl₂·NO₂ (IV) and PhSNa-10% aq. NaOH-EtOH, warmed for 5 min., give the sulphide, m.p. 86°, which with H₂O₂-AcOH affords 4-chloro-2-nitrodiphenylsulphone, m.p. 121°, converted by piperidine (*loc. cit.*) into 2-nitro-4-, m.p. 172°, and 4-chloro-2-, m.p. 121°, -piperidinodiphenylsulphone, and (III). 4:2':5'-Trichloro-2-nitrodiphenylsulphone, m.p. 131° [sulphide, m.p. 106—107°, from 2:5:1-C₆H₃Cl₂·SNa and (IV)], similarly gives 2':5'-dichloro-2-nitro-4-, m.p. 172°, and 4:2':5'-trichloro-2-, m.p. 153°, -piperidinodiphenylsulphone, and (III). (I) (R = NH₂) and piperidine (45 min.) afford 4-chloro-2-, m.p. 152°, and an equal amount of 2-nitro-4-, m.p. 137°, -piperidinobenzenesulphonamide, and (III). 4-Chloro-2-nitrophenyl thiobenzoate, m.p. 124°, and Cl₂-AcOH-H₂O give 4:2:1-C₆H₃Cl·NO₂·SO₂Cl (80—90% yield), converted by 2 mols. of cold piperidine into 4-chloro-2-nitrobenzenesulphonylpiperidide, m.p. 138°, which with piperidine (45 min.) gives 4-chloro-2-, m.p. 105°, and 2-nitro-4-, m.p. 121°, -piperidinobenzene-sulphonylpiperidide (equal amounts) and (III). 2:4-

Dinitrophenyl thiobenzoate and $\text{Cl}_2\text{-AcOH-H}_2\text{O}$ or the corresponding sulphide and $\text{Cl}_2\text{-H}_2\text{SO}_4$ afford 2 : 4 : 1- $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-SO}_2\text{Cl}$, m.p. 102° , converted by 2 mols. of cold piperidine-EtOH into 2 : 4-dinitrobenzenesulphonylpiperidide, m.p. 130° . The latter or 2 : 4 : 1- $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-SO}_2\text{-NH}_2$, and excess of piperidine for $\frac{1}{2}$ hr. give 2 : 4-dinitro-1-piperidinobenzene, whilst $p\text{-C}_6\text{H}_4\text{Me-SNa}$ (*loc. cit.*) yields 2 : 4- $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-S-C}_6\text{H}_4\text{Me}$ (IV) and $p\text{-C}_6\text{H}_4\text{Cl-SNa}$ give 4 : 4'-dichloro-2-nitrodiphenyl sulphide, m.p. 158° , oxidised to the -sulphone, m.p. 133° , which with $\text{H}_2\text{SO}_4\text{-KNO}_3$ affords 4 : 4'-dichloro-2 : 3'-dinitrodiphenylsulphone, m.p. 162° . This and $p\text{-C}_6\text{H}_4\text{Me-SNa}$ give (II), but 2 mols. of piperidine in dioxan at room temp. yield solely 4-chloro-2 : 3'-dinitro-4'-piperidinodiphenylsulphone, m.p. 140° , converted by PhSNa into (II). (I) ($\text{R} = p\text{-C}_6\text{H}_4\text{Me}$) (V) and NaOMe or NaOEt give 4-chloro-2-nitro-anisole and -phenetole, the latter with 4-chloro-2-ethoxyphenyl- p -tolylsulphone, m.p. 105° , also. (V) and $\text{Na } p\text{-tolyl}$ oxide in p -cresol, or refluxing in NH_2Ph (5 hr.), give 4-chloro-2-nitrophenyl p -tolyl ether and 5-chloro-2- p -toluenesulphonyldiphenylamine, m.p. 121° , respectively. Good yields of sulphonyl chlorides are obtained from p -tolyl, o -nitrophenyl, and benzyl disulphoxides and $\text{Cl}_2\text{-AcOH-H}_2\text{O}$ (*loc. cit.*); Et ethylxanthate affords ethanesulphonyl chloride (cf. Douglass *et al.*, A., 1938, II, 305).

A. T. P.

Determination of *cis-trans* isomerism. C. WINGAND and E. MERKEL (Med. u. Chem., 1936, 3, 320—324; Chem. Zentr., 1937, i, 567).—Comparison of the ultra-violet absorption of *cis*- and *trans*-olefinic isomerides with sterically related cyclic compounds is suggested. Thus *cis*- and *trans*-stilbene spectrally resemble 4 : 5-diphenylglyoxaline and 2-phenylindene, respectively.

A. H. C.

Clarification of the spatial configuration of di- p -tolyl by means of the action of sulphur. L. SZPERL [with A. FAJNBERG] (Congr. int. Quim. pura apl., 1934, 9, IV, 233—237; Chem. Zentr., 1936, ii, 4211).— $\text{CH}_2\text{Ph-O-CH}_2\text{R}$ ($\text{R} = \text{Me, Et}$) react slowly with S in CO_2 at $170\text{--}180^\circ$ to give dehydrogenation and condensation products, *e.g.*, BzOH , $(\text{CHR})_2$, $(\text{CHPh})_2$, RCO_2H , tetraphenylthiophene. $\text{CH}_2\text{Ar-OH}$ and S (0.05—0.1 atom) give $(\text{CH}_2\text{Ar})_2\text{O}$. Di- p -tolyl (1 mol.) and S (1 atom) at $210\text{--}230^\circ/35$ hr. afford hydrocarbons, $(\text{CH}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{Me})_2$, m.p. $210\text{--}212^\circ$, and $(\text{C}_6\text{H}_4\text{-[CH}_2\text{]}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{Me})_2$, m.p. $310\text{--}315^\circ$.

H. B.

Alkylation of naphthalene with alcohols and boron fluoride. Mechanism of the reaction. C. C. PRICE and J. M. CISKOWSKI (J. Amer. Chem. Soc., 1938, 60, 2499—2502).—Passing BF_3 into C_{10}H_8 in Pr^iOH , cyclohexanol (I), or Bu^iOH gives exothermally and rapidly good yields of (mainly) β -substitution products (mono-, di-, and tri-). In $\text{CH}_2\text{Ph-OH}$ mainly 1- with some 2- $\text{C}_{10}\text{H}_7\text{-CH}_2\text{Ph}$ is formed. cycloHexene and BF_3 also give 2-cyclohexylnaphthalene, but this cannot be the reaction with the alcohol, since (I) is unchanged by BF_3 . A reaction mechanism is postulated involving fission of the alcohol- BF_3 complex to give alkyl cations. With C_6H_6 derivatives BF_3 gives only p -compounds; in the Friedel-Crafts reaction m -derivatives are formed owing to the reversibility of the

reaction by the following changes: $\text{PhR} \leftrightarrow p\text{-C}_6\text{H}_4\text{R}_2 \leftrightarrow 1 : 2 : 4\text{-C}_6\text{H}_3\text{R}_3 \leftrightarrow m\text{- and } o\text{-C}_6\text{H}_4\text{R}_2$.

R. S. C.

Compounds of naphthalenesulphinic acids with their sodium and potassium salts. M. P. BALFE and (Mrs.) W. G. WRIGHT (J.C.S., 1938, 1490—1491).—Naphthalene-1- (I), new m.p. 87° (cf. Thomas, J.C.S., 1909, 95, 342), and -2-sulphinic acid (II), new m.p. 98° , through the chlorides, afford the respective *Me* esters, m.p. 44° and 42° (cf. Otto *et al.*, A., 1893, i, 343). Careful addition of 5N-HCl to (I) in $\text{Na}_2\text{SO}_3\text{-H}_2\text{O}$ ppts. a salt, m.p. 75° , consisting of (I) and its Na salt in equimol. proportions (+2 H_2O); it separates from EtOH with 1 mol. of solvent (lost at 95°), m.p. 48° . (I) and 0.5N-KOH-EtOH at 0° afford a similar "K H salt" (+2EtOH), m.p. 38° , which loses 1 EtOH at 93° . It decomposes at $>100^\circ$ to SO_2 and C_{10}H_8 , which is not characteristic of either (I) or its K salt. The Na salt of (II) and excess of 5N-HCl give a similar salt, becoming slightly yellow at 150° (chars $>150^\circ$); the K H salt of (II) becomes yellow $>150^\circ$, and finally chars without melting. These new "H salts" are probably compounds rather than mixtures; they can be crystallised in unchanged ratio from solvents in which acid or alkali salt is insol.; they remain stable after 18 months. Similar salts of acid and K salt in equimol. proportions are obtained from BzOH and from $o\text{-OH-C}_6\text{H}_4\text{-CO}_2\text{H}$ [m.p. 260° (decomp.)] (cf. Ross *et al.*, A., 1938, I, 189).

A. T. P.

Raman effect and problems of constitution. XII. Condensed dicyclic hydrocarbons resembling naphthalene.—See A., 1938, I, 556.

Mechanism of high-temperature hydrogenation of aromatic hydrocarbons. I. Anthracene and phenanthrene hydrides. II. Octahydrides of anthracene, and their formation. E. I. PROKOPETZ. III. Composition of the liquid product formed together with symmetrical octahydroanthracene, and the isomerisation of the latter. E. I. PROKOPETZ, A. V. PAVLENKO, and S. M. BOGUSLAVSKAJA. IV. Mutual transformations of anthracene octahydrides. V. Composition of liquid perhydroanthracene. E. I. PROKOPETZ and S. M. BOGUSLAVSKAJA (J. Appl. Chem. Russ., 1938, 11, 822—834, 835—839, 840—846, 847—849, 850—852).—I. The products of hydrogenation (160—180 atm.; MoS_2 catalyst) of anthracene (I) are 9 : 10-di- (II), 1 : 2 : 3 : 4-tetra- (III), *s*-octa- (IV), and perhydroanthracene (V) (solid and liquid); the amount of H_2 combining rises as the temp. is raised from 300° to 450° . Under analogous conditions phenanthrene (VI) yields 1 : 2 : 3 : 4-tetra-, 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octa- (VII), and perhydrophenanthrene (VIII); dihydrophenanthrene is not obtained. The temp. at which max. yields of any desired hydride are obtained are determined, and the prep. of the pure hydrides is described.

II. (IV), as obtained by low-temp. ($250\text{--}265^\circ$) hydrogenation of (I), (II), or (III), is contaminated with as-octahydroanthracene [=benzo-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydronaphthalene] (IX), m.p. 63.5° , oxidised by KMnO_4 to $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$.

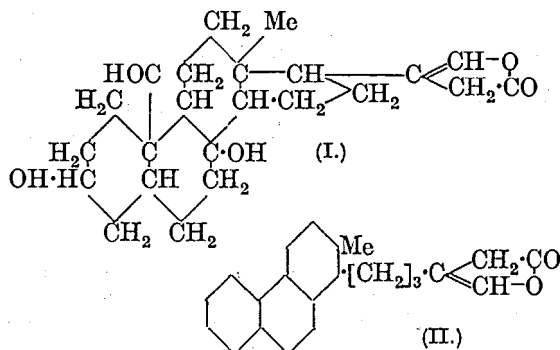
III. The liquid product of catalytic hydrogenation

of (I) at 350° consists of solid and liquid (V), (IV), (IX), and (VII). (IV) undergoes transformation into (VII) in presence, but not in absence, of MoS₂.

IV. The reaction (IV) \rightleftharpoons (IX) is demonstrated at 335°, in presence of MoS₂.

V. Liquid (V) is dehydrogenated (Ni-Al catalyst) to a mixture of (I) and (VI). It is hence concluded that (VIII) is a product of high-temp. hydrogenation of (I). R. T.

Strophanthidin dehydrogenation product, C₂₁H₁₆. E. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 2306—2307).—The hydrocarbon, m.p. 296°, obtained from strophanthidin (I) by Se (Jacobs *et al.*, A., 1934, 1359) has absorption max. at 2720, 2800, 2980, and 3150, and weaker max. at 3200, 3400, and 3600 Å., and is identical with 7-methyl-1:2-2':1'-naphthafuorene, m.p. 301° (slow heating) (lit. 334—336°, preheated bath), formed by way of (II). During aromatisation of the various steroids the Me at C₁₃



may thus be eliminated, used for conversion of a C₅ into a C₆ ring, used to form a new cyclopentane ring, or may migrate. The hydrocarbons from cholesterol and ergosterol are probably 7-methyl-5-isobutyl- and 5- α -methylisobutyl-1:2-2':1'-naphthafuorene, respectively. R. S. C.

β -Hydroxyphenylethylamines and their transformations. VI. Preparation of β -hydroxyphenylethylamines with free phenolic hydroxyl group. G. HAHN and K. STIEHL (Ber., 1938, 71, [B], 2154—2162).—Dropwise addition of 50% NaOH to *o*-OH·C₆H₄·CHO and MeNO₂ in MeOH at 0° gives *o*-OH·C₆H₄·CH:CH·NO₂ (yield 34.5%), reduced (general method: PtO₂ in AcOH containing sufficient H₂SO₄ to give the H sulphate of the base) to *o*-OH·C₆H₄·CH₂·CH₂·NH₂ in 79% yield. *o*-OH·C₆H₄·CHO and MeNO₂ in presence of NH₃Me·OAc in MeOH afford 3-nitro-2-*o*-hydroxyphenyl-5:6-benzyl:2-pyran, m.p. 183—184°, reduced (PtO₂ in AcOH) to the NH₂-compound [H sulphate, m.p. 227—228° (decomp.); hydrochloride (also +1H₂O), decomp. 260°]. *m*-OH·C₆H₄·CHO, MeNO₂, and NaOH give *m*-OH·C₆H₄·CH:CH·NO₂ in 66% yield, reduced to β -*m*-hydroxyphenylethylamine, decomp. 103—104° [picrate, m.p. 173—175°; H sulphate, m.p. 108—111° (decomp.)], in 72.5% yield. β -3-Hydroxy-4-methoxyphenylethylamine, m.p. 151—153°, is almost quantitatively obtained from the corresponding nitrostyrene. Vanillin, MeNO₂, NH₂Me, HCl, and Na₂CO₃ in MeOH give 4:3-OH·C₆H₃(OMe)·CH:CH·NO₂ in 84% yield,

reduced to β -4-hydroxy-3-methoxyphenylethylamine, m.p. 158—159° [H sulphate, m.p. 151—152° (decomp.)]; picrate, m.p. 198—199°, in 84.6% yield. *p*-OAc·C₆H₄·CHO, MeNO₂, and KOH in MeOH-H₂O give ω -nitro-*p*-acetoxystryrene (I), m.p. 158—159° (yield 11%), *p*-OH·C₆H₄·CHO, and *p*-OH·C₆H₄·CH:CH·NO₂ (II). β -*p*-Hydroxyphenylethylamine [H sulphate, m.p. 123—125° (decomp.)] is obtained in 85% yield from (I) or in 80% yield from (II). The above amines can also be prepared by catalytic hydrogenation of the corresponding OH·CHAr·CN. The conversion of aldehydes into ω -nitrostyrenes is fully discussed. H. W.

Complex formation between polynitro-compounds and aromatic hydrocarbons and bases. VI. Interaction between *s*-trinitrobenzene and some aromatic bases. (Miss) B. R. HAMILTON and D. L. HAMMICK (J.C.S., 1938, 1350—1352; cf. A., 1938, II, 268).—Stabilities of the coloured complexes of *s*-C₆H₃(NO₃)₃ with *o*-, *m*-, and *p*-C₆H₄R·NH₂ (R = Me, Cl, Br), NH₂Ph, NHPhMe, NPhMe₂, NHPh₂, NPh₃, and α -C₁₀H₇·NH₂ have been compared at 25° and 60° by measurement of the increase of colour of solutions of *s*-C₆H₃(NO₃)₃ in CCl₄ as more base is added (cf. A., 1936, 1453). λ at max. absorption is recorded for the complexes with the last 6 bases. The heats of interaction, calc. by means of the van 't Hoff isochore, are ~2 kg.-cal. (cf. *loc. cit.*). The stabilities of the complexes diminish from C₆H₄Me·NH₂ through NH₂Ph and C₆H₄Br·NH₂ to C₆H₄Cl·NH₂, and run roughly parallel with the basicities of the bases. H. G. M.

***p*-Alkyldimethylanilines.** W. C. DAVIES and F. L. HULBERT (J.S.C.I., 1938, 57, 349—351).—Convenient methods for prep. of these bases in a pure state are given. *p*-Dimethylamino-ethyl-, b.p. 104°/16 mm. (incorrectly described by Heumann and Wiernik, A., 1887, 1039) (methiodide, m.p. 218°), *n*-propyl-, b.p. 116—118°/16 mm. (methiodide, m.p. 195.5°), *n*-butyl-, b.p. 137°/16 mm. (methiodide, m.p. 199.5°), and *iso*-butylbenzene, b.p. 128—130°/16 mm. (methiodide, m.p. 177.5°), are prepared by methylation (Me₂SO₄) of the corresponding primary amines (from rearrangement of the *sec.* alkylaniline). Dimethylcumidine, *p*-dimethylaminosec.-butylbenzene, b.p. 130—132°/16 mm. (methiodide, m.p. 167°), and *p*-dimethylaminotert.-butylbenzene, b.p. 124—126°/16 mm. (methiodide, m.p. 196°), are prepared from the *p*-alkylbenzene by nitration, reduction, and methylation. The Fittig method (*p*-C₆H₄Br·NMe₂-RBr-Na) and the Friedel-Crafts method (NPhMe₂-RBr-AlCl₃) are unsatisfactory.

Reductive fission in the antipyrine series. W. KROHS (Med. u. Chem., 1936, 3, 310—319; Chem. Zentr., 1937, i, 601).—Antipyrine, its 4-Me and 4'-NH₂-derivatives with H₂ (100 atm.) and a Ni contact at 180° give mainly NHPh·COPr (I), NHPh·CO·CHMeEt, and *p*-NH₂·C₆H₄·NH·COPr, respectively. (I) is similarly produced from 1-phenyl-3-methyl-5-pyrazolone. Hexahydroantipyrine [1-cyclohexyl-2:3-dimethyl-5-pyrazolone], usefully characterised as the sulphate, resembles antipyrine therapeutically; reduction of its 4-NO₂- to the 4-NH₂-derivative and

di-*N*-methylation of this affords *hexahydropyrimidone*, m.p. 77—79°, which is less toxic than pyrimidone.

A. H. C.

Action of water on aromatic carbimides.

C. NÄGELI, A. TYABJI, L. CONRAD, and F. LITWAN (Helv. Chim. Acta, 1938, **21**, 1100—1126; cf. A., 1933, 602).—Aromatic acids substituted by electron acceptors (NO_2 , halogen, or acyl) can be transformed into their chlorides and thence by NaN_3 (in COMe_2 — H_2O , dioxan, or MeOH —dioxan) into the azides, which are converted by heating in PhMe or xylene into the carbimides; after removal of solvent these are dissolved in moist Et_2O or COMe_2 with 1% of H_2O (absence of acids and bases). The carbamide can usually be filtered off and the amine obtained from the filtrate. The highest yields of diarylcarbimides are obtained from the carbimides with cold H_2O in heterogeneous system; with boiling H_2O there is more amine. A marked fall of carbamide yield occurs in the sequence 3:5-dinitro-, *o*-nitro-, and 2:4-dinitro-phenylcarbimide. The amine yield increases at the expense of carbamide with increasing dilution of the carbimide reacting in homogeneous system with H_2O , but becomes diminished to the advantage of the carbamide with increasing H_2O content of the homogeneous system. In homogeneous and heterogeneous system PhNCO , its *p*- and *m*- OMe -, and its *p*- Me derivative are converted by H_2O almost exclusively into diarylcarbimides. In both systems carbimides substituted by NO_2 give increased yields of amine. The effect of a substituent in promoting the formation of amine is: *p*- $\text{OMe} < p\text{-Me} < \text{H} < m\text{-OMe} < m\text{-NO}_2 < p\text{-NO}_2 < 3:5\text{-(NO}_2)_2 < o\text{-NO}_2 < 2:4\text{-(NO}_2)_2 < 2:4:6\text{-(NO}_2)_3$. Ability to form diarylcarbamide with H_2O is not shown by 2:4-di- or 2:4:6-tri-nitrophenylcarbimide. The yields of diarylcarbimides obtained by boiling the carbimides and the corresponding arylamine in C_6H_6 — PhMe for 1 hr. usually decrease with decreasing basicity of the arylamine, i.e., in the above sequence of substituents. In the simultaneous presence of about 2.5 times the equiv. amount of H_2O (in COMe_2 containing 1% of H_2O) and of an equiv. amount of the amine corresponding with the carbimide the yield of carbamide diminishes with decreasing basicity of this amine, i.e., in the above sequence. With carbimides substituted by nucleophilic residues (electron donors) and with PhNCO itself the reaction between carbimide and added amine is practically quant. The amounts of diarylcarbimides obtained by boiling for one hr. solutions of nuclear-substituted carbimides with one and the same amine (*p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$) usually increase in the above sequence of substituents. The low val. for *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NCO}$ is outstanding. The terminal members of the carbimide series, the OMe -, Me -, and *m*- NO_2 -derivatives, and PhNCO itself on the one hand, and 2:4-dinitrophenylcarbimide on the other hand, can be converted completely into the corresponding amines by conc. HCl whereas the intermediate members give greater or smaller quantities of carbamides. The amounts of urethane formed after 3 or 10 min. are a measure of the rate of addition of H_2O to carbimide and hence for the first step in the reaction of both substances. Substituents influencing the rate of reaction of aromatic carbimides with

MeOH can be arranged in accordance with the nature and position in the ring in the same sequence as given above. The results are fully discussed. H. W.

Reaction of aromatic carbimides with aromatic amines. C. NÄGELI, A. TYABJI, and L. CONRAD (Helv. Chim. Acta, 1938, **21**, 1127—1143).—With regard to the action of ArNCO on NH_2Ar in aromatic hydrocarbons, the influence of substituents on the activity of the NCO is: *p*- $\text{OMe} < p\text{-Me} < \text{H} < m\text{-OMe} < m\text{-NO}_2 < p\text{-NO}_2 < 3:5\text{-(NO}_2)_2 < 2:4\text{-(NO}_2)_2$. Reactivity of the NH_2Ar is denoted by the same sequence in the reverse sense. *o*- NO_2 -groups in arylcarbimides and arylamines diminished the rates of addition by "steric" hindrance. This restriction does not oppose the general influence of NO_2 -groups on the reactivity of the amines but reduces the reactivity of *o*- to that of *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NCO}$. The yields of diarylcarbimides cannot be reproduced with samples of differing origin; minute amounts of unrecognised impurities increase the yields very greatly. The rate of reaction between ArNCO and NH_2Ar can be very greatly increased by the addition of small amounts of certain org. acids or of $\text{C}_6\text{H}_5\text{N}$. Dicarboxylic acids of all types are unsuitable if the possibility exists that they may be present in non-polar solvents in the dihydroxylactone form. It is improbable that carboxylic anhydrides, anilides, or mixed carboxylic-carbamic anhydrides are responsible for the catalysis, which may be an effect of polarisability. An electronic interpretation of the change is given. The following appear new: 2:4-dinitrobenzazide, m.p. 68° (decomp.), and -phenylcarbimide, m.p. 63°; *Bu*^a 2:4-di-, m.p. 91°, and 2:4:6-tri-, m.p. 135°, -nitrophenylcarbimate, 2:4:6-trinitrobenzazide, m.p. 98° (decomp.); *m*-methoxybenzazide, m.p. 22.5°, decomp. 61°, and -phenylcarbimide, b.p. 96°/18 mm.; *p*-toluazide, m.p. 28°; diphenylcarbimides: 2- NO_2 -, m.p. 170°; 2-nitro-4'-phenyl-, m.p. 208°; 2-, m.p. >300°, 3-, m.p. >300°, and 4-nitro-4'-aminophenyl-, m.p. >300°; 4-nitro-4'-phenyl-, m.p. 259°; 2:4-(NO_2)₂-, m.p. 176°; 2:4-dinitro-4'-phenyl-, m.p. 219°; 3:5-dinitro-4'-phenyl-, m.p. 227°; 2:3'-(NO_2)₂-, m.p. 228°; 2:4'-(NO_2)₂-, m.p. 270—275° (decomp.); 3:4'-(NO_2)₂-, m.p. 273°; 2-, m.p. 145°, 3-, m.p. 170°, and 4-nitro-3'-methoxy-, m.p. 252°; 2:4:2'-(NO_2)₃-, m.p. 218°; 2:4:3'-(NO_2)₃-, m.p. 205°; 2:4:4'-(NO_2)₃-, m.p. 260°; 2:4-dinitro-3'-methoxy-, m.p. 193°; 2:4:6:3'-(NO_2)₄-, m.p. 164°; 3:5:2'-(NO_2)₃-, m.p. 245°; 3:5:3'-(NO_2)₃-, m.p. 232°; 3:5:4'-(NO_2)₃-, m.p. 265°; 3:5-dinitro-3'-methoxy-, m.p. 215°; 2:4:3:5'-(NO_2)₄-, m.p. 215°; 4- OMe -, m.p. 186—190°; 4:3'-(OMe)₂-, m.p. 153°; 4-methoxy-4'-methyl-, m.p. 236°; 3'-nitro-4-methoxy-, m.p. 195°; 3'-methoxy-4-methyl-, m.p. 181°; 4-*p*-aminophenyl-, m.p. >300°; 3- OMe -, m.p. 155°; 3:3'-(OMe)₂-, m.p. 171°. Phenylbenzylcarbimides (substituents invariably in the Ph nucleus): 2- NO_2 -, m.p. 170°; 4- NO_2 -, m.p. 185—195°; 2:4-(NO_2)₂-, m.p. 173—174°; 3:5-(NO_2)₂-, m.p. 195—201°; 4- OMe -, m.p. 158°; 3- OMe -, m.p. 155°.

H. W.

Chemical and physiological examination of ethylenic amines and diamines. G. BENOTT and R. HERZOG (Bull. Sci. Pharmacol., 1935, **42**,

34—43; 102—109; Chem. Zentr., 1936, ii, 4208).—CHPhBr·CH₂Br and NHEt₂ at 180° give 20% of (probably) crude CHPh·CH·NEt₂, whilst CHPhBr·CHMeBr at 145° affords CPhBr·CHMe. The unstable CH₂Ph·CHBr·CH₂Br (passes readily into CHPh·CH·CH₂Br) and CHPhBr·CH₂·CH₂Br [from CHPh·CH·CH₂·OH and HBr (2 mols.) at 100°] with NHEt₂ at 130—140° give γ -diethylamino- α -phenyl- Δ^a -propene, b.p. 146—147°/25 mm. (hydrochloride, m.p. 141°; picrate, m.p. 130°); with NH₂Me, methylcinnamylamine, b.p. 148—150°/30 mm. (Bz derivative, m.p. 187·5°), results. Similarly CPhMeBr·CH₂Br affords γ -diethylamino-, b.p. 120—125°/13 mm. (hydrochloride, m.p. 113°), and γ -methylamino- β -phenyl- Δ^a -propene, b.p. 108—112°/15 mm. [hydrochloride, m.p. 140°; picrate, m.p. 131°; (?) methiodide, m.p. 160°]; CPhMeBr·CHMeBr gives γ -diethylamino-, b.p. 133—136°/18 mm., and γ -methylamino- β -phenyl- Δ^a -butene, b.p. ~120°/14 mm. (hydrochloride, m.p. 165°; picrate, m.p. 164°); CPhEtBr·CHMeBr yields δ -methylamino- γ -phenyl- Δ^b -pentene, b.p. 163—166°/70 mm. (hydrochloride, m.p. 157°). These amines possess nicotine- and ephedrine-like actions.

Successive treatment of NMe₂·CHPh·CH₂·OH with SOCl₂ (in CHCl₃) and NH₂Me (in C₆H₆ at 130°) gives *r*- β -methylamino- α -dimethylamino- α -phenylethane, b.p. 128—134°/14 mm. (hydrochloride, m.p. 111°). *r*- β -Methylamino- α -dimethylamino- α -phenylpropane, b.p. 127°/15 mm. (hydrochloride, m.p. 24°), the *d*-form, b.p. 124—126°/14 mm. (hydrochloride, m.p. 244°), and *l*-form, b.p. 124°/14 mm. (hydrochloride, m.p. 245°; mono-, m.p. 189—190°, and *di*-, m.p. 143°, -picrate; methiodide, m.p. 214°), are similarly prepared starting from the ephedrine. *d*- α -Methylamino- β -dimethylamino- α -phenylpropane, b.p. 122°/20 mm. (dihydrochloride, m.p. 229°; picrate, m.p. 187·5°), is obtained from NMe₂·CHMe·CHPhCl.

CH₂Cl·CHPh·CO₂Et and NHEt₂ in C₆H₆ at 135° give *Et* β -dimethylamino- α -phenylpropionate, b.p. 147°/18 mm. (hydrochloride, m.p. 143°), reduced (Bouveault) to γ -dimethylamino- β -phenylpropyl alcohol, b.p. 148°/18 mm.; the chloride (hydrochloride, m.p. 174°) and NH₂Me afford α -methylamino- γ -dimethylamino- β -phenylpropane, b.p. 128°/11—12 mm. (hydrochloride, m.p. 229·5—230°). These diamines cause lowering of blood pressure. H. B.

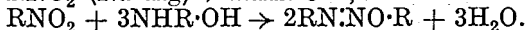
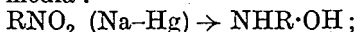
Urethanes as local anæsthetics. IV. Alkyl *N*-*p*-aminobenzylcarbamates. R. L. SHRINER and J. M. CROSS (J. Amer. Chem. Soc., 1938, 60, 2338—2340; cf. A., 1933, 1044).—A series of *p*-aminobenzylurethane hydrochlorides have only slight anæsthetic action when injected subcutaneously or applied topically and are irritant. Me *p*-nitrophenylacetate is prepared from the acid in 83·5% yield by dry HCl·MeOH. *p*-Nitrophenylacetazide, m.p. 45° (decomp.), unstable, with the appropriate alcohol gives *Me*, m.p. 104—105°, *Et*, m.p. 115—116°, *Pr*^a, m.p. 89—90°, *Pr*^b, m.p. 107—108°, *Bu*^a, m.p. 62—63°, *Bu*^b, m.p. 59—60°, *sec*-*Bu*, m.p. 62—63°, *n*-, m.p. 49—50°, and *iso*-*amyl*, an oil, α -methyl-*n*-butyl, m.p. 50—51°, α -ethyl-*n*-propyl, m.p. 50—51°, β -methyl-*n*-butyl, *n*-hexyl, *n*-heptyl, oils, *n*-octyl, m.p. 48—50°, and α -methyl-*n*-heptyl, m.p. 64—65°, *N*-*p*-

nitrobenzylcarbamate. These with H₂-PtO₂ in abs. EtOH followed by dry HCl give *Me*, decomp. 177—178°, *Et*, decomp. 160—161°, *Pr*^a, decomp. 153—155°, *Pr*^b, decomp. 177—178°, *Bu*^a, decomp. 156—158°, *Bu*^b, decomp. 160—162°, *sec*-*Bu*, decomp. 153—154°, *n*-, decomp. 152—154°, and *iso*-*amyl*, decomp. 157—159°, α -methyl-*n*-butyl, decomp. 140—146°, α -ethyl-*n*-propyl, decomp. 149—150°, β -methyl-*n*-butyl, decomp. 152—153°, *n*-hexyl, decomp. 157—158°, *n*-heptyl, decomp. 157—158°, *n*-octyl, decomp. 159—161°, and α -methyl-*n*-heptyl, decomp. 147—148°, *p*-aminobenzylcarbamate hydrochloride. M.p. are corr. R. S. C.

Derivatives of 3:3'-diaminodiphenyl. E. A. CALDERON (Rev. Fac. Cienc. Quím. La Plata, 1938, 11, 27—36).—(*m*-NH₂·C₆H₄)₂ (I), like (*p*-NH₂·C₆H₄)₂ (II), gives colours with various aldehydes, and insol. salts with SO₄²⁻, CrO₄²⁻, and WO₄²⁻. Congo-red (III) and its isomeride prepared from (I) have analogous properties, whence it is concluded that the quinonoid structure of (III) does not extend to the Ph₂ nucleus. (I) cannot be oxidised by PbO₂ in CHCl₃ or H₂O. (I) and (II) give analogous condensation products with phenanthraquinone.

F. R. G.

Azoxy-compounds. Mechanism of their formation during the reduction of nitro-compounds with sodium amalgam. V. O. LUKASCHVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 137—140).—From comparisons of the rates of formation of azoxy- by reduction of NO₂-compounds with NHA·OH and with Na-Hg in N₂, the following mechanism is proposed for reductions in alkaline media:



A. LI.

Tertiary amides. E. JOLLES and B. BINI (Gazzetta, 1938, 68, 510—515).—NPh₂·COCl (I) and NHPPh·NH₂ heated in C₆H₆ give triphenylsemicarbazide, new m.p. 151—152°, oxidised by FeCl₃ in EtOH to benzeneazocarboxydiphenylamide, new m.p. 157°, further oxidised by AcO₂H to the benzene-azoxy-compound, m.p. 163°. *p*-Chlorophenylhydrazino-, m.p. 164°, and *p*-chlorobenzene-azo-, m.p. 151°, and -azoxy-carboxydiphenylamide, m.p. 162°, are prepared similarly. Phenylhydrazinocarboxyphenylmethylamide, m.p. 134°, is obtained from NPhMe·COCl; neither the latter nor (I) reacts with *p*-C₆H₄Cl·NH·NH₂. *p*-C₆H₄Me·N·N·CO·NH₂ and AcO₂H give *p*-toluene-azoxycarboxylamide, m.p. 181·5° (decomp.). *p*-C₆H₄Me·NH·NH₂ does not react appreciably with (I).

E. W. W.

Alkaline scission of some azoxycarboxylic derivatives. E. JOLLES (Gazzetta, 1938, 68, 504—509).—2:4-Dibromobenzeneazocarboxy-*p*-bromoanilide (A., 1936, 979) is hydrolysed by alkali, *p*-C₆H₄Br·NH₂ being liberated. With MeOH·KOH, benzeneazoxycarboxydiphenylamide gives NHPPh₂ (also liberated, in brominated form, by CHCl₃·Br), or, in presence of β -C₁₀H₇·NH₂, benzeneazo- β -naphthol; under the latter conditions, *p*-chlorobenzeneazoxycarboxydiphenylamide yields NHPPh₂ and the azo- β -naphthol. E. W. W.

Reactions of aliphatic diazohydrocarbons. II. Action of azo-esters. E. JOLLES [with M. RIDI and L. GIORDANO] (Gazzetta, 1938, 68, 496—504).— CH_2N_2 and $\text{PhN}_2\cdot\text{CO}\cdot\text{NH}_2$ (I) in Et_2O give a compound, $\text{C}_{17}\text{H}_{18}\text{ON}_6$, m.p. 174.5° (decomp.) (stable to many reagents), from which dil. H_2SO_4 liberates NH_2Ph and CH_2O , and which with 25% MeOH — KOH gives a substance, $\text{C}_{17}\text{H}_{15}\text{ON}_5$, m.p. 152.5° . From the $p\text{-C}_6\text{H}_4\text{Cl}$ and $p\text{-C}_6\text{H}_4\text{Me}$ analogues of (I), products $\text{C}_{17}\text{H}_{16}\text{ON}_6\text{Cl}$ (*sic*), m.p. 181.5° , and $\text{C}_{19}\text{H}_{22}\text{ON}_6$, m.p. 161° , respectively, are obtained. CH_2N_2 and $\text{PhN}_2\cdot\text{CO}\cdot\text{NHPh}$ give a substance, $\text{C}_{14}\text{H}_{13}\text{ON}_3$, m.p. $206\text{—}210^\circ$. $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{NH}_2$ and ClCO_2Me yield *Me p-chlorophenylhydrazinoformate*, m.p. $123\text{—}124^\circ$, oxidised by FeCl_3 to the corresponding azo-compound, m.p. 63° , which with CH_2N_2 gives a product, $\text{C}_{40}\text{H}_{48}\text{O}_8\text{N}_8\text{Cl}_4$, m.p. $120\text{—}140^\circ$ (decomp.). *Me β -naphthylhydrazinoformate*, m.p. 153° , is oxidised (KMnO_4) to the azo-compound, an oil, which also reacts with CH_2N_2 . E. W. W.

Influence of constitution on the stability of monoazo-dyes from 1-amino- β -naphthyl ethers and their sulpho-derivatives. H. E. FIERZ-DAVID and R. DUPONT (Helv. Chim. Acta, 1938, 21, 1367—1370).—The hydrolysis of a series of substituted 4-benzeneazo-2-ethoxy- α -naphthylamines to NH_3 and the corresponding α -naphthols has been examined under strictly comparable conditions (cf. A., 1938, II, 317). SO_3H in the benzenoid nucleus in the *meta* position has little and in the *para* position rather more influence on the instability of the dye, which is very greatly increased by *o*- SO_3H . The most stable pigments are those which do not contain SO_3H in the benzenoid component. The dye obtained from 1:2:5- $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{SO}_3\text{H})_2$ (I) and 1:2- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OEt}$ is less stable than that derived from (I) and 1:2:6- or 1:2:7- $\text{NH}_2\cdot\text{C}_{10}\text{H}_5(\text{OEt})\cdot\text{SO}_3\text{H}$. The dye from (I) and 1:2:8- $\text{NH}_2\cdot\text{C}_{10}\text{H}_5(\text{OEt})\cdot\text{SO}_3\text{H}$ is among the least stable. SO_3H in the 6 or 7 position to N_2 has very little influence or may be stabilising, whereas it renders the dye very unstable if in position 8. A reason cannot at present be advanced.

H. W.

Oxidative fission in the antipyrine series. M. BOCKMÜHL (Med. u. Chem., 1936, 3, 294—319; Chem. Zentr., 1937, i, 600).— HNO_2 reacts with antipyrine or 4-nitrosoantipyrine to yield "antipyrine nitrite" [α -oximinoacetacet-(β' -nitroso- α' -phenyl- β' -methylhydrazide)] (I), m.p. 132° (decomp.), slowly hydrolysed by alkali or NH_2OH to β -nitroso- α -phenyl- β -methylhydrazine (II), m.p. $46\text{—}47^\circ$. Reduction (SnCl_2) of (I) gives 4-aminoantipyrine; cyclisation is also effected by heating its (β -)phenylhydrazone, m.p. 191° (decomp.), with $\text{NHPH}\cdot\text{NH}_2$ to yield (II) and 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone, m.p. 155° . Benzoylation of (II) affords the α -Bz derivative, m.p. 130° , reduced to α -benzoyl- α -phenyl- β -methylhydrazine, m.p. 88° . α -Nitroso- β -benzoyl- α -phenyl- β -methylhydrazine, m.p. 111° , is obtained from $\text{NHPH}\cdot\text{NMeBz}$. Similarly pyrimidone and HNO_2 give first a blue colour and then "pyrimidone nitrite" [probably $\alpha\beta$ -diketobutyr-(β' -nitroso- α' -phenyl- β' -methylhydrazide) β -hydrate] (III), m.p. $91\text{—}92^\circ$ (also obtainable from melubrin, novalgin, or 4-hydroxy-

antipyrine), which diazotises NH_2Ph and yields azo-dyes with, e.g., $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$. It is quickly isomerised by alkali to *hydroxymethylmalon- β -nitroso- α -phenyl- β -methylhydrazidic acid*, $\text{NO}\cdot\text{NMe}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}$ [*Na salt* (+ $2\text{H}_2\text{O}$)]; reduction (loss of NO) gives the α -phenyl- β -methylhydrazidic acid, m.p. 170° . Excess of NaOH converts (III) into (II) and $\text{OH}\cdot\text{CMe}(\text{CO}_2\text{H})_2$, m.p. 143° . Reduction (SnCl_2 , $\text{Na}_2\text{S}_2\text{O}_4$, etc.) of (III) gives 4-hydroxyantipyrine, m.p. 182° . (III) is converted by HCO_2H into a compound, probably $(\text{CH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}\cdot\text{NPh}\cdot\text{NHMe})_2$, m.p. 270° (decomp.), which with NaOH gives $\alpha\delta$ -dihydroxybutane- $\alpha\alpha\delta\delta$ -tetracarboxylic acid, m.p. 180° . Cautious sublimation of this affords the *di- δ -lactone* of $\alpha\alpha'$ -dihydroxyadipic acid. $\text{NHPH}\cdot\text{NH}_2$ and (III) at moderate temp. give the compound, $\text{NHPH}\cdot\text{NH}\cdot\text{CMe}(\text{OH})\cdot\text{CO}\cdot\text{CO}\cdot\text{NPh}\cdot\text{NMe}\cdot\text{NO}$, m.p. 107° , and the β -phenylhydrazone (IV), m.p. 139° (decomp.), of $\alpha\beta$ -diketobutyr-(β' -nitroso- α' -phenyl- β' -methylhydrazide). 4-Benzeneazo-, m.p. 155° , and 4-hydroxy-, decomp. 212° (cf. lit.), 1-phenyl-3-methyl-5-pyrazolone are obtained from (IV) and $\text{NHPH}\cdot\text{NH}_2$ at higher temp. A. H. C.

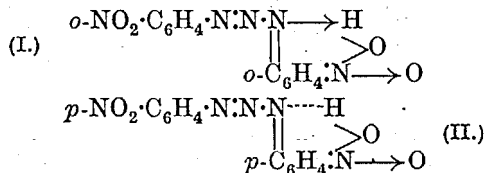
Action of hydrazine bases on some substituted carbamides. E. JOLLES and G. RAGNI (Gazzetta, 1938, 68, 516—521).— $\text{NPhMe}\cdot\text{CO}\cdot\text{NH}_2$ and $\text{NHPH}\cdot\text{NH}_2$ (I) at $185\text{—}190^\circ$ give diphenylcarbazine (II), and a substance, $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_5$ [*bis*(phenylhydrazino-carboxylamide) (?)], m.p. 225° ; $\text{NPh}_2\cdot\text{CO}\cdot\text{NH}_2$ also gives (II). $\text{NPh}_2\cdot\text{CO}\cdot\text{NHPH}$ forms $\text{NHPH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPH}$ (III). Neither NNN' -triphenyl- N' -methylcarbamide, m.p. 106° (from NHPHMe and $\text{NPh}_2\cdot\text{COCl}$), nor $\text{CO}(\text{NPhEt})_2$ reacts with (I). With $\text{NHPH}\cdot\text{CO}\cdot\text{NHMe}$, $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{NH}_2$ yields $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPH}$; $\text{NHPH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ gives phenylurazole, also obtained from (II); and $\text{NHPH}\cdot\text{CO}_2\text{Et}$ gives (III). E. W. W.

New aromatic fluoro-derivatives. II. (SRA.) A. C. DE DEGIORGI and E. V. ZAPPI (Anal. Asoc. Quím. Argentina, 1938, 26, 41—47).—1:3:5- $\text{C}_6\text{H}_3\text{F}(\text{NO}_2)_2$ (A., 1935, 1229) with Sn and HCl yields 1-fluoro-3:5-diaminobenzene dihydrochloride. 3:5-Dichloro- and 3-chloro-5-nitro-benzenediazonium chlorides with 40% HBF_4 give the benzenediazonium borofluorides, decomp. $170.5\text{—}180^\circ$ and $190\text{—}195^\circ$, respectively, which when heated yield 1:3-dichloro-5-fluoro-, a liquid, and 1-chloro-3-fluoro-5-nitro-benzene, b.p. $198\text{—}200^\circ$, respectively. F. R. G.

Normal *o*-carboxybenzenediazonium hydroxide. G. ILLARI (Gazzetta, 1938, 68, 532—542).—The product from diazotised $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $\text{EtOH}\cdot\text{KOH}$ under CO_2 gives, when acidified, BzOH , MeCHO , and the substance, $(\text{C}_7\text{H}_6\text{O}_2\text{N}_2)_n$ [$o\text{-C}_6\text{H}_4\text{C}(\text{CO}\cdot\text{O})\text{NH}\cdot\text{NH}\cdot\text{NH}_2$] (I), m.p. 245° (decomp.) (Ag salt). This with $\text{SnCl}_2\text{—HCl}$ yields the dihydrochloride, $\text{C}_{14}\text{H}_{15}\text{O}_4\text{N}_4\text{Cl}_2$ [converted by NaOAc into the substance, $\text{C}_{14}\text{H}_{14}\text{O}_4\text{N}_4\cdot\text{H}_2\text{O}$, m.p. 185° (decomp.) (loses H_2O at 120°)], and with $\text{NaHCO}_3\text{—KI—I}$ forms the substance $\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_4\text{I}$, m.p. 200° (decomp.), which with NaOH followed by acid regenerates (I). E. W. W.

Dimorphous forms of nitrodiazoamino-compounds. F. P. DWYER (J.S.C.I., 1938, 57, 357–358).—The existence of dimorphous forms of 4-nitro-2'- and -4'-methyldiazoaminobenzene (Mehner, A., 1902, i, 576) has been confirmed on the purified substances. In each case the two forms have the same colour, and react at the same rate with dil. KOH; thus no conflict arises with the normal and *aci*-forms of the dinitrodiazoamino-compounds recently described (*infra*).

Normal and *aci*-forms of dinitrodiazoamino-compounds. F. P. DWYER (J.S.C.I., 1938, 57, 351—357).—By crystallisation of purified 2 : 2'- and 4 : 4'-dinitrodiazoaminobenzene from EtOH or COMe₂ containing NH₃, red and purple *cryst. forms*, considered to have the respective *aci*-structures (I) and (II), were obtained. The true triazen forms,



lemon-yellow, were obtained by crystallisation from EtOH containing NH_3 and NH_4Cl . The *aci*-forms react instantly with dil. KOH, yielding the dark-coloured K salts, whilst the triazen forms react much more slowly. *aci*-2:2'-Dinitrodiazoaminobenzene has m.p. 193° (shrinking), re-solidifying with m.p. 199° ; the triazen form has m.p. 199° (slight decomp.; orange at 193°). With MeI in MeOH-KOH both give 2:2'-dinitromethyl diazoaminobenzene, m.p. $115-116^\circ$. *aci*-4:4'-Dinitrodiazoaminobenzene, m.p. $224-225^\circ$ (decomp.) (slow), or $245 \pm 2^\circ$ (sudden heating), and the triazen form, m.p. 230° or $245 \pm 2^\circ$, form a compound, brownish-purple, m.p. 235° or $250 \pm 2^\circ$, by crystallisation of equal parts from COMe_2 . The pure triazen forms of the 2:3', 2:4', and 3:4'-(NO_2)₂-compounds are also described, but only mixtures of the coloured *aci*-forms with these have been isolated. *aci*-Forms could not be isolated from diazoaminobenzene, its Me, Me_2 , NO_2 -, 3:3'-(NO_2)₂-, or nitromethyl derivatives, or from dinitrodiazoaminocompounds containing diazoaminoazo-impurity. The *aci*-form is involved in $\text{Mg}(\text{OH})_2$ -lake formation.

Azo-group as a chelating group. III. Metallic derivatives of hydroxytriazens. M. ELKINS and L. HUNTER (J.C.S., 1938, 1346—1350).—The salts of the hydroxytriazens (cf. Bamberger *et al.*, A., 1898, i, 20) are co-ordination compounds (general formula as annexed), being readily sol. in org. solvents and usually melting $<200^{\circ}$. The parent hydroxytriazens (of less thermal stability than their salts) are also considered to be largely in a similar co-ordinated form. Methods of synthesis are discussed. The following are described: 1-hydroxy-3-phenyl-1-methyltriazen, m.p. $72-73^{\circ}$ (lit. $69-70^{\circ}$) [Cu^{II} , m.p. $159-160^{\circ}$ (lit. 156°)]; *Ni*, m.p. 182° (*dipyridino*-compound, m.p. $\sim 145^{\circ}$ after loss of $\text{C}_2\text{H}_5\text{N}$ at $\sim 100^{\circ}$), *Fe}^{\text{III}}*, m.p. 176° , *Co}^{\text{III}}*, m.p. 165° , and *tripyridinocobaltous* compound, m.p. $116-120^{\circ}$]; 1-hydroxy-3-o-tolyl-1-methyltriazen, m.p. 51° (*Cu}^{\text{II}}*, m.p. 169°).

170°, *Ni*, m.p. 208°, *Fe*^{III}, m.p. 168°, *Co*^{II}, m.p. 171°, and *Co*^{III}, m.p. 136°, compounds); 1-hydroxy-3-m-tolyl-1-methyltriazen, m.p. 74° [*Cu*^{II}, m.p. 140—141°, *Ni*, m.p. 180°, *Co*^{II}, m.p. ~125°, if rapidly, and m.p. 155° if slowly, heated (tripyrindino-compound, m.p. 130—135°), and *Co*^{III}, m.p. 158°, compounds]; 1-hydroxy-3-p-tolyl-1-methyltriazen, m.p. 115—116° (*Cu*^{II}, m.p. 187°, *Ni*, m.p. 227°, *Fe*^{III}, m.p. 176°, *Co*^{II}, m.p. 184—186°, and *Co*^{III}, m.p. 156°, compounds); 1-hydroxy-3-β-naphthyl-1-methyltriazen, m.p. 143—144° [*Cu*^{II}, m.p. 212°, *Ni*, m.p. 216° (dipyrindino-compound, loses C₅H₅N at ~90°), *Fe*^{III}, m.p. 155°, and *Co*^{III}, m.p. 170°, compounds]; 1-hydroxy-1:3-diphenyltriazen, m.p. 127—128° [*Cu*^{II}, m.p. 190—192°, *Ni*, m.p. 211° (dipyrindino-compound), *Fe*^{III}, m.p. 156° (impure), *Co*^{II}, m.p. 175° (dipyrindino-compound, m.p. 120—125° after loss of C₅H₅N at ~115°), and *Co*^{III}, m.p. 108—109°, compounds]; 1-hydroxy-1-phenyl-3-p-tolyltriazen, m.p. 131° [*Cu*^{II}, m.p. 191°, *Ni*, m.p. 222° (dipyrindino-compound), *Fe*^{III}, m.p. 155°, *Co*^{II}, m.p. 184°, and *Co*^{III}, m.p. 117° softening at 105°, compounds]. The triazens explode when heated above the m.p.

H. G. M.

Exchange of hydrogen atoms between nitrophenols and water. II. Chemistry of the reaction. M. KOIZUMI and T. TITANI (Bull. Chem. Soc. Japan, 1938, 13, 595—600, 641—643; cf. A., 1938, 1, 315).—In alkaline solution the exchange of nuclear H of $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ takes place chiefly by substitution of hydroxylic H of the neutral phenol mols. by nuclear H of the phenoxide ions. At low alkali concns., the reaction between phenoxide ions and H_2O cannot be excluded entirely. J. D. R.

J. D. R.

Reaction of isobutene and diisobutene with phenol, with and without scission of C-C linkings. V. N. IPATIEV, H. PINES, and B. S. FRIEDMAN (J. Amer. Chem. Soc., 1938, **60**, 2495—2497).—Diisobutene (I), PhOH, and a little 96% H_2SO_4 first in the cold and then at 65° give *p*- $\text{CH}_2\text{Bu}^i\text{CMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ (II) and 2:4-di-(α - γ -tetramethyl-*n*-butyl)phenol, b.p. 210—215°/29 mm., but no Bu^i derivatives (cf. Natelson, A., 1934, 999). However, with much H_2SO_4 at 85° some *p*- $\text{C}_6\text{H}_4\text{Bu}^i\text{OH}$ (III) is obtained. With H_3PO_4 there is no reaction at <150°; at 150° a little (II) and (III) are formed. With H_3PO_4 at 140° or 200° (II) gives (III), 2:4:1- $\text{C}_6\text{H}_3\text{Bu}_2\cdot\text{OH}$ (IV), PhOH, and C_6H_{18} . *iso*- C_4H_8 and PhOH in H_3PO_4 at 100° give good yields of (III) and (IV). With HNO_3 -AcOH (III) gives the 2:6-(NO_2)₂-derivative, but (IV) gives 4:6-dinitro-2-*tert*-.butylphenol, also prepared by nitration of 4-nitro-2-*tert*-.butylphenol, m.p. 138.5—139.5° (from *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, C_4H_8 , and H_3PO_4 at 100°). R. S. C.

R. S. C.

Synthesis, structure, properties, and derivatives of diisobutyl- $[p$ - α - γ -tetramethyl- n -butyl]-phenol. J. B. NIEDERL [with R. A. SMITH, J. B. WHITMAN, M. ALTAMURO, W. H. BOWMAN, P. W. HODGES, H. JOSEPH, E. KATZMAN, G. C. KEEFFE, V. NIEDERL, L. SCHRIER, J. SIMON, and R. SHERMAN] (Ind. Eng. Chem., 1938, **30**, 1269—1274).—The prep. of p -CH₂Bu[•]·CMe₂·C₆H₄·OH (PhOH coeff. 158) in 17-g. and 1900-lb. batches, its properties, and oxidation to p -OH·C₆H₄·CO₂H (1—2% yield) by NaOH-CuO are described. The following are prepared by

standard reactions. *p*- $\alpha\alpha\gamma\gamma$ -Tetramethyl-*n*-butylphenyl Me (I), b.p. 272°, and Et (II), b.p. 280°, CH_2Ph , m.p. 106°, and $\text{C}_{10}\text{H}_7\cdot\text{CH}_2$ ether, m.p. 99°, acetate, b.p. 122—124°/1 mm., benzoate, m.p. 81—83°, and *p*-nitrobenzoate, m.p. 115°, phenyl-, m.p. 145—147°, and α -naphthyl-urethane, m.p. 116°. 5-Methoxy-, m.p. 155° (oxime, m.p. 169°; dioxime, m.p. 183°), and 5-ethoxy-2- $\alpha\alpha\gamma\gamma$ -tetramethyl-*n*-butyl-*p*-benzoquinone, m.p. 135° [obtained from (I) and (II), respectively, with a little *p*- $\text{OR}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ by $\text{CrO}_3\text{--AcOH}$]. 2-Chloro-, m.p. 27—29°, 2:6-dichloro-, m.p. 44—46°, 2-bromo-, m.p. 30—32°, 2-nitro-, an oil (*Na* salt; benzoate, m.p. 98—99°), 2-bromo-6-nitro-, m.p. 136°, 2:6-dinitro-, m.p. 68°, 2-amino- (III) (hydrochloride, m.p. 210°), and 2:6-di(hydroxymethyl)-, m.p. 70° (*Me* ether, m.p. 105°; tribenzoate, m.p. 108—111°), 4- $\alpha\alpha\gamma\gamma$ -tetramethyl-*n*-butylphenol. 4-Nitro-, m.p. 161°, 2-chloro-, m.p. 98°, 2:5-dichloro-, m.p. 105°, 4-acetamido-, m.p. 165°, 4-methoxy-, m.p. 115°, and 4-sulpho-, m.p. 305° (decomp.), 2'-hydroxy-5'- $\alpha\alpha\gamma\gamma$ -tetramethyl-*n*-butylazobenzene. 2'-Nitro-2-hydroxy-4'-methyl-5- $\alpha\alpha\gamma\gamma$ -tetramethyl-*n*-butylazobenzene, m.p. 137°. 4'-Benzamido-2-hydroxy-2':5'-diethoxy-5- $\alpha\alpha\gamma\gamma$ -tetramethyl-*n*-butylazobenzene, m.p. 165°. 2-Hydroxy-5- $\alpha\alpha\gamma\gamma$ -tetramethyl-*n*-butylbenzene-1-azo-2'-toluene-5'-azo-2''-toluene, m.p. 136°, and -1-azo-1'-naphthalene-4'-sulphonic acid, m.p. 315° (decomp.). Diphenyl-4:4'-bis(azo-2'-hydroxy-5'- $\alpha\alpha\gamma\gamma$ -tetramethyl-*n*-butylbenzene), m.p. 168°. *p*- $\alpha\alpha\gamma\gamma$ -Tetramethyl-*n*-butylphenoxycetic acid, m.p. 108—109°. 5- $\alpha\alpha\gamma\gamma$ -Tetramethyl-*n*-butylsalicylic acid, m.p. 157—158° (*Ac* derivative, m.p. 99—100°). *p*- $\alpha\alpha\gamma\gamma$ -Tetramethyl-*n*-butylphenol-sulphonic (*Na* salt; *Me* ether) and -disulphonic acid (*Na*₂ salt). 5- $\alpha\alpha\gamma\gamma$ -Tetramethyl-*n*-butylsalicylaldehyde, m.p. 50°, b.p. 296° (phenylhydrazine, m.p. 169°; semicarbazone, m.p. 228°; 2:4-dinitrophenylhydrazine, m.p. 185°). By diazotisation and hydrolysis (III) gives 4- $\alpha\alpha\gamma\gamma$ -tetramethyl-*n*-butylpyrocatechol, m.p. 107°, which is bactericidally very active. R. S. C.

Tyraminesulphuric acid. M. LOEFER and J. PARROD (Bull. Soc. Chim. biol., 1938, 20, 1117—1118).—*p*- β -Aminoethylphenyl *H* sulphate [tyraminesulphuric acid], m.p. $\sim 320^\circ$ (decomp.), prepared from tyramine, its hydrochloride, and $\text{NH}_2\cdot\text{SO}_3\text{H}$ (ratio 3:1:3) at 160°/20 hr., is readily hydrolysed (dil. acid at 100°). It may be of importance in the metabolism of tyramine. A. L.

Preparation of resorcinol.—See B., 1938, 1265.

New form of resorcinol.—See A., 1938, I, 562.

Derivatives of 1:2:3:4-tetrahydroxybenzene. V. Synthesis of parsley apiole and derivatives. W. BAKER and R. I. SAVAGE (J.C.S., 1938, 1602—1608; cf. A., 1935, 80).—1:2:3:4- $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{CO}_2\text{H}$ (I), 10% NaOH , and $\text{Me}_2\text{SO}_4\text{--MeOH}$ at 100° (bath)/1 hr. give an improved yield of 2-hydroxy-3:4-dimethoxybenzoic acid (II), decarboxylated to 1:2:3- $\text{C}_6\text{H}_3(\text{OH})(\text{OMe})_2$, which with aq. $\text{K}_2\text{S}_2\text{O}_8\text{--NaOH}$ for 36 hr. (alkaline) affords 1:4:2:3- $\text{C}_6\text{H}_2(\text{OH})_2(\text{OMe})_2$ (III), new m.p. 84—85° (diacetate, m.p. 54°) (cf. A., 1931, 1411), converted by $\text{Me}_2\text{SO}_4\text{--NaOH}$ into 1:2:3:4- $\text{C}_6\text{H}_2(\text{OMe})_4$, m.p. 88—89°. (II) and $\text{K}_2\text{S}_2\text{O}_8\text{--NaOH}$ give 2:5-dihydroxy-3:4-dimethoxybenzoic acid, m.p. 171° [loses CO_2 at 200°

to give (III)], which with aq. $\text{KOH--Me}_2\text{SO}_4\text{--COMe}_2$ affords 2:3:4:5-tetramethoxybenzoic acid, m.p. 87—88°, prepared previously only from natural sources. (I) and $\text{CH}_2\text{SO}_4\text{--aq. NaOH--COMe}_2$ in coal gas at room temp.—100° afford 2-hydroxy-3:4-methylenedioxybenzoic acid (IV), m.p. 235° (evolves CO_2) (*Ac* derivative, m.p. 165°), decarboxylated in quinoline + Cu chromite (A., 1931, 598) at 180° to pyrogallol CH_2 ether (V), m.p. 65°, which with aq. $\text{K}_2\text{S}_2\text{O}_8\text{--NaOH}$ yields methylenedioxyquinol, m.p. $\sim 180^\circ$ (some decomp.) (diacetate, m.p. 104°). $\text{Me}_2\text{SO}_4\text{--KOH--MeOH}$ then affords 1:4-dimethoxy-2:3-methylenedioxybenzene, m.p. 77—77.5°, identical with parsley apione from apiole (cf. isomeric dill apione, *loc. cit.*). (IV) and aq. $\text{K}_2\text{S}_2\text{O}_8\text{--NaOH}$, after 36 hr., yields 2:5-dihydroxy-3:4-methylenedioxybenzoic acid, m.p. 250° (decomp.), converted by aq. $\text{Me}_2\text{SO}_4\text{--KOH--COMe}_2$ at 50°, then at b.p., into apiolic acid, m.p. 173°, identical with that from parsley apiole, each with Br--AcOH giving 1:2-dibromo-3:6-dimethoxy-4:5-methylenedioxybenzene, m.p. 97—98° (cf. Ciamician and Silber, A., 1888, 1100). (V), allyl bromide, and $\text{K}_2\text{CO}_3\text{--COMe}_2$, refluxed for 8 hr., afford 2:3-methylenedioxyphenyl allyl ether, b.p. 139—140°/24 mm., which rearranges at 220—240° to 2-hydroxy-3:4-methylenedioxy-1-allylbenzene, b.p. 155—156°/20 mm. This and aq. $\text{K}_2\text{S}_2\text{O}_8\text{--NaOH}$ give 2:5-dihydroxy-3:4-methylenedioxy-1-allylbenzene, and the 2:5-(*OMe*)₂-compound, m.p. 28.5—29° [Br-derivative dibromide, m.p. 80—80.5° (cf. lit.)], is identical with parsley apiole. The monobenzyloxy-pyrogallol of Einhorn *et al.* (A., 1898, i, 577; cf. Zetzsche *et al.*, A., 1926, 67) is the 1-*O*-Bz derivative, m.p. 140°, since with $\text{MeI--K}_2\text{CO}_3\text{--COMe}_2$, or in poor yield by CH_3N_3 , it gives 2:3-dimethoxyphenyl benzoate, m.p. 56°; also obtained from 1:2:3- $\text{C}_6\text{H}_3(\text{OH})(\text{OMe})_2$ and $\text{BzCl--C}_6\text{H}_5\text{N}$ (cf. Herzig and Pollak, A., 1904, i, 808). *o*-Vanillin and 6% aq. H_2O_2 in 2*N*- NaOH in coal gas give 2:3:1- $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{OMe}$, m.p. 41—42°, b.p. 151°/24 mm. 2:3-Dihydroxy-4-methoxybenzaldehyde has m.p. 118—119° (cf. Mauthner, A., 1936, 1109; Baker *et al.*, A., 1938, II, 183). (IV) in AcOH with Br , or HNO_3 (d 1.42) at 40°, affords 5-bromo-, m.p. 255° (decomp.) (separates + AcOH , lost at 100°), or 5-nitro-, m.p. 295° (decomp.), 2-hydroxy-3:4-methylenedioxybenzoic acid, respectively. 4-Methyldaphnetin and CH_2SO_4 in 10% NaOH--COMe_2 at 70° for 4 hr. give the CH_2 ether, m.p. 226°. 4-Methyldaphnetin Me_2 ether and AcOH--HNO_3 (d 1.5) afford the 5- (or 6-) NO_2 -derivative, m.p. 138—139°.

A. T. P.

Halogenation of phenolic ethers and anilides. IX. Influence of fluorine and of alkyl groups. B. JONES (J.C.S., 1938, 1414—1417; cf. A., 1936, 719).—Comparative velocity coeffs. for the chlorination of $\text{C}_6\text{H}_4\text{X}\cdot\text{OR}$ [$\text{X} = p\text{-F}$ and $\text{R} = \text{Pr}^i$, CH_2Ph , $p\text{-C}_6\text{H}_4\text{Y}\cdot\text{CH}_2$ ($\text{Y} = \text{Me}$, Et , Cl , Br , NO_2); $\text{X} = o\text{-F}$ and $\text{R} = \text{CH}_2\text{Ph}$, $p\text{-C}_6\text{H}_4\text{Y}\cdot\text{CH}_2$ ($\text{Y} = \text{Me}$, Br , NO_2); $\text{X} = p\text{-Cl}$ and $\text{R} = \text{CH}_2\text{Ph}$, $p\text{-C}_6\text{H}_4\text{Y}\cdot\text{CH}_2$ ($\text{Y} = \text{Me}$, Et , Pr^i , Bu^i), 2:4- and 3:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2$; $\text{X} = o\text{-Cl}$ and $\text{R} = p\text{-C}_6\text{H}_4\text{Y}\cdot\text{CH}_2$ ($\text{Y} = \text{Me}$, Et , Bu^i), $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}_2$] and of $p\text{-C}_6\text{H}_4\text{F}\cdot\text{NH}_2$ ($\text{Y} = \text{Ac}$, Bz , PhSO_2) in 99% AcOH at 20° are recorded. Comparison with previous velocity data shows that for *p*-halogeno-ethers the reactivities are in the ratio

F : Cl : Br = 191 : 100 : 103. Introduction of alkyl into the benzyl radical increases the rates of halogenation of $C_6H_4X \cdot O \cdot CH_2Ph$ ($X = Cl$ or F) to the same extent in the case of *p*-Me, *p*-Et, *p*-Pr^{*b*}, and *p*-Bu^{*γ*}; a further increase is obtained by introduction of a second alkyl ($3:4 < 2:4-Me_2$). The following are described. *p*-Fluorophenyl ethers: benzyl, m.p. 55·5°, *p*-methyl-, m.p. 69°, *p*-ethyl-, m.p. 65°, *p*-chloro-, m.p. 58°, *p*-bromo-, m.p. 66°, *o*-, m.p. 62°, and *p*-, m.p. 74·5°, -nitro-benzyl, Pr^{*b*}, b.p. 73°/18 mm. *o*-Fluorophenyl ethers: benzyl, m.p. 42°, *p*-methyl-, m.p. 66°, *p*-bromo-, m.p. 66°, and *p*-nitro-, m.p. 84·5°, -benzyl. *p*-Chlorophenyl ethers: *p*-ethyl-, m.p. 82·5°, *p*-isopropyl-, m.p. 79·5°, and *p*-tert.-butyl-, m.p. 92°, 2:4-, m.p. 81°, and 3:4-, m.p. 89°, -dimethyl-benzyl. *o*-Chlorophenyl ethers: *p*-ethyl-, m.p. 79°, *p*-tert.-butyl-, m.p. 63°, and *m*-methyl-, m.p. 77°, b.p. 183°/13 mm., -benzyl. Benzenesulphon-*p*-fluoroanilide has m.p. 110°.

H. G. M.

Vitamin-E. Ethers of duroquinol. E. FERNHOLZ and J. FINKELSTEIN (J. Amer. Chem. Soc., 1938, 60, 2402—2404).—Duroquinol (I) with the appropriate alkyl halide and an equiv. of KOH in hot EtOH gives the di- and mono-alkyl ethers (cf. A., 1938, II, 186). The cetyl ether is, however, obtained from the dicetyl ether, m.p. 88—89°, by 1 mol. of $AlCl_3$ in C_6H_6 ; 2 mols. of $AlCl_3$ gives (I). Duroquinol sec.-Bu ether acetate, m.p. 62—63°, duroquinol didodecyl, m.p. 79—80°, dioctadecyl, m.p. 95—97°, di-(α -methyl-n-octadecyl), m.p. 75—76°, and di-(β -methyl-n-octadecyl) ether, m.p. 76—78°, are described. Hydrogenation (PtO_2) of $C_{17}H_{35}COOMe$ in AcOH gives *n*-nonadecan- β -ol, m.p. 48—49° (*p*-nitrobenzoate, m.p. 95·5°), converted by gaseous HBr at 110—120° into the bromide, b.p. 170°/0·05 mm. $CMcNa(CO_2Et)_2$ and $C_{16}H_{33}I$ in EtOH give *Et_2* methylcetylmalonate, b.p. 185—190°/1 mm., converted by KOH-EtOH and subsequent thermal decomp. into *Et* α -methylstearate, b.p. 161—163°/1 mm., and thence by $H_2-Cu-Cr_2O_3$ at 250°/133 atm. into β -methyl-n-octadecyl alcohol, m.p. 32—33°, which with red P-I at 170—180° gives the iodide, b.p. 185° (bath)/0·05 mm.

R. S. C.

Chlorination of *o*- and *p*-aminophenol. Theory of substitution regularities. W. THIELACKER (Ber., 1938, 71, [B], 2065—2070).—Contrary to Holleman, the directive action of NH_2 exceeds that of OH and it is possible to chlorinate 4:1- $NH_2 \cdot C_6H_4 \cdot OH$ at $C_{(3)}$. Since NH_2 must be protected by conversion into $NHAc$ whereby its directive power is lessened, it is necessary also to acetylate OH.

p-NHAc· C_6H_4 ·OAc (I) is converted by Cl_2 in EtOH-free $CHCl_3$ at room temp. into 3-chloro-4-acetamidophenyl acetate (II), m.p. 130°, hydrolysed by conc. HCl at 100° to 4:3:1- $NH_2 \cdot C_6H_3Cl \cdot OH$, m.p. 160° (darkening). Chlorination of (I) in hot $CHCl_3$ is accompanied by the formation of more tar but gives chiefly (II) with small amounts of a product hydrolysed to a trichloro-4-acetamidophenol, m.p. 184—185°. Addition of I is not helpful. In cold AcOH only (II) is formed in poor yield and addition of I is disadvantageous. Chlorination of (I) or, preferably, of (II) in $C_2H_2Cl_4$ at 100° gives 3:5-dichloro-4-acetamidophenyl acetate, m.p. 182° (with some hexachloro- Δ^1 -cyclohexene-3:6-dione, m.p. 86—87°), hydrolysed by

conc. HCl at 100° to 4:3:5:1- $NH_2 \cdot C_6H_2Cl_2 \cdot OH$, m.p. 154°. *o*-NHAc· C_6H_4 ·OAc is transformed by Cl_2 in $CHCl_3$ at room temp. into 5-chloro-2-acetamidophenyl acetate, m.p. 163—164°, hydrolysed by conc. HCl at 100° to 5-chloro-2-acetamido-, m.p. 189—190°, or 2-amino-phenol, m.p. 153°.

H. W.

Manufacture of *o*- and *p*-N-substituted aminoarylsulphones.—See B., 1938, 1268.

Arylidene derivatives of 4:4'-diaminodiphenylsulphone.—See B., 1938, 1363.

Naphthalene derivatives. I. Action of alkali sulphites on *o*-diazonaphtholsulphonic acids. A. KREBSER and F. VANNOTTI (Helv. Chim. Acta, 1938, 21, 1221—1233).—Replacement of the N_2 group of diazonaphtholsulphonic acids by SO_3H by means of Na_2SO_3 occurs only when N_2 and OH are attached to $C_{(1)}$ and $C_{(2)}$, respectively. The change is due to the primary formation of a sulphite adduct. There is thus a close analogy with the 1-azo-, 1-nitroso-, and 1-sulpho-naphthols, which also give additive compounds with $NaHSO_3$, whereas this behaviour is not shown by members of the 2:1-series. Na 1-diazo- β -naphthol-4-sulphonate (I) and Na_2SO_3 give a red-orange, non-homogeneous additive product which ultimately leaves a residue of (I) when crystallised from H_2O . Na 6-nitro-1-diazo- β -naphthol-4-sulphonate gives the stable adduct (II), $C_{10}H_5O_9N_3S_2Na_2 \cdot 3H_2O$. With aq. Na_2SO_3 containing Cu and $CuSO_4$ at 100° (I) gives N_2 and 2:1:4-OH· $C_{10}H_5(SO_3H)_2$ [Na_2 (+3 H_2O) salt], hydrolysed by boiling dil. H_2SO_4 to 2:4-OH· $C_{10}H_6 \cdot SO_3H$. Similarly the N_2 compound from 1:2:6- $NH_2 \cdot C_{10}H_5(OH) \cdot SO_3H$ is transformed by boiling aq. Na_2SO_3 into 2:6-OH· $C_{10}H_6 \cdot SO_3H$ and 2:1:6-OH· $C_{10}H_5(SO_3H)_2$ (Na_2 salt, anhyd. and +3 H_2O). 6-Bromo-1-diazo- β -naphthol-4-sulphonic acid is transformed by successive action of NaOH + Na_2SO_3 and Na_2SO_3 -Cu- $CuSO_4$ into 2:6:1:4-OH· $C_{10}H_4Br(SO_3H)_2$ [Na_2 (+1 H_2O) salt], whence 2:6:4-OH· $C_{10}H_5Br \cdot SO_3H$ [Na (+1·5 H_2O) salt]. (II) is converted into 2:6:1:4-OH· $C_{10}H_4(NO_2)(SO_3H)_2$ [Na_3 (+8 H_2O and +6 H_2O), Na_2 (+2 H_2O), K_2 , $(NH_4)_2$, and Ba_2 salts], transformed by boiling 10% H_2SO_4 into 2:6:4-OH· $C_{10}H_5(NO_2) \cdot SO_3H$. 2:6:1:4-OH· $C_{10}H_4(NH_2)(SO_3H)_2$ [Na (+1 H_2O) salt] and 2:6:4-OH· $C_{10}H_5(NH_2) \cdot SO_3H$ are described. 2-Diazo- α -naphthol-4-sulphonic acid and 4:8-disulphonic acid are converted by Na_2SO_3 into varying amounts of azonaphtholsulphonic acids with the corresponding hydrazines and 1-naphtholsulphonic acids.

H. W.

Secondary alcohol from β -apo-2-carotenal; homologues of axerophthol (vitamin-A). P. KARRER, A. RÜEGGER, and A. GEIGER (Helv. Chim. Acta, 1938, 21, 1171—1174; cf. A., 1937, II, 378).— β -apo-2-Carotenal is converted by $MgEtBr$ into the sec. alcohol, 3-hydroxy-19-(2':6':6'-trimethyl- Δ^1 -cyclohexenyl)-4:8:13:17-tetramethyl- Δ .4:6:8:10:12:14:16:18-nonadecaoctaene, m.p. 86°, the absorption spectrum of which is nearly identical with that of β -apo-2-carotenol. Close correspondence is therefore to be expected between vitamin- A_2 if correctly formulated as β -apo-5-carotenol (Gillam *et al.*, A., 1938, III, 315) and the alcohol obtained by

reduction of the ketone (I) of Batty *et al.* (A., 1938, II, 126). Reduction of (I) with $\text{Al}(\text{OPr}^{\beta})_3$ gives a non-homogeneous product unsuitable for spectral comparison.

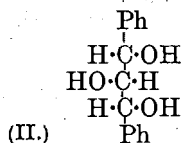
H. W.

Reducing and condensing action of alkali benzylates on carbonyl compounds and α -unsaturated alcohols. P. MASTAGLI (Ann. Chim., 1938, [xi], 10, 281—377).—Mainly a detailed account and generalisation of work already reported (A., 1937, II, 102, 415; 1938, II, 100). The reaction of aldehydes or ketones with boiling $\text{CH}_2\text{Ph}\cdot\text{OH}$ in presence of KOH or NaOH to give the alcohol and PhCHO is general. Part of the PhCHO produced undergoes the Cannizzaro reaction; part condenses with the unchanged original aldehyde, giving $\text{CHPh}\cdot\text{CR}\cdot\text{CHO}$, which is reduced to $\text{CH}_2\text{Ph}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{OH}$ by oxidation of more PhCHO to BzOH ; if the original aldehyde was $\text{CHAr}\cdot\text{CR}\cdot\text{CHO}$, the unsaturated alcohol initially produced is reduced to $\text{CH}_2\text{Ar}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{OH}$ if KOH is used, but not if NaOH is used. In some cases the original aldehyde condenses with the alcohol produced and the resultant $\text{CHR}\cdot\text{CR}\cdot\text{CH}_2\cdot\text{OH}$ is then reduced at the expense of more PhCHO . In some of the simplest cases, ArCHO , where reduction of the alcohol is impossible, a little H_2 is evolved. Occasionally unexpected reactions occur: *e.g.*, $\text{CH}_2\text{Ph}\cdot\text{CHO}$ gives $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CHPh}$ and $s\text{-C}_6\text{H}_5\text{Ph}_3$ as well as $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{OH}$ (*allophanate*, m.p. 162°; also obtained from $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$, PhCHO , and KOH). Additional examples described are the conversion of $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ into $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$, piperonal into $\text{CH}_2\text{O}\cdot\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OH}$, $\text{Ph}[\text{CH}_2]_2\cdot\text{CHO}$ into $\text{CH}(\text{CH}_2\text{Ph})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ (I) and $\epsilon\text{-phenyl-}\beta\text{-benzyl-n-amyl alcohol}$ (II), b.p. 224°/15 mm. (*allophanate*, m.p. 110°), $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ into (I) and (II), and COPhMe into $\text{Ph}[\text{CH}_2]_2\cdot\text{CHPh}\cdot\text{OH}$, $\alpha\gamma\text{-diphenyl-n-butyl alcohol}$, b.p. 202°/15 mm. (*allophanate*, m.p. 148°), and $\text{CH}(\text{CH}_2\text{Ph})_2\cdot\text{CHPh}\cdot\text{OH}$. $\text{CHPh}\cdot\text{CR}\cdot\text{CH}_2\cdot\text{OH}$ with $\text{KOH}\cdot\text{CH}_2\text{Ph}\cdot\text{OH}$ gives $\beta\text{-heptyl-}$, b.p. 186°/15 mm. (*allophanate*, m.p. 139°), -octyl- , b.p. 198°/15 mm. (*allophanate*, m.p. 138°), -nonyl- , b.p. 212°/17 mm. (*allophanate*, m.p. 136°), $\Delta^0\text{-nonenyl-}$, b.p. 212°/17 mm. (*allophanate*, m.p. 127°), and $\text{-decyl-cinnamyl alcohol}$, b.p. 221°/15 mm., m.p. 42° (*allophanate*, m.p. 137°). The following are incidentally described: *cumyl phenylurethane*, m.p. 62°, and *allophanate*, m.p. 201°; $\beta\text{-n-amyl-nonyl formate}$, b.p. 156°/14 mm., *acetate*, b.p. 163—164°/17 mm., *propionate*, b.p. 172°/15 mm., and *isobutyrate*, b.p. 180°/20 mm., and *Me*, b.p. 144—145°/17 mm., *Et*, b.p. 149°/17 mm., *Pr* ^{β} , b.p. 150°/15 mm., and *Bu*, b.p. 174°/20 mm., *ether*; $\zeta\text{-chloro-}$, b.p. 146—148°/15 mm., -bromo- , b.p. 154—156°/15 mm., and $\text{-iodo-methyl-n-tridecane}$, b.p. 170—171°/19 mm.; $\beta\text{-benzyl-n-heptyl formate}$, b.p. 168°/16 mm., *acetate*, b.p. 173°/15 mm., *propionate*, b.p. 182—184°/20 mm., and *isobutyrate*, b.p. 182—183°/17 mm., and *Me*, b.p. 146—147°/17 mm., *Et*, b.p. 152°/15 mm., *Pr* ^{β} , b.p. 156°/17 mm., and *Bu*, b.p. 178°/19 mm., *ether*; $\beta\text{-ethyl-}$, m.p. 147°, -butyl- , m.p. 155°, and $\text{-hexyl-cinnamyl allophanate}$, m.p. 142°. Hydrogenation (Ni under pressure) of $\text{CHPh}\cdot\text{C}(\text{C}_5\text{H}_{11})\cdot\text{CHO}$ at 90° gives $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{C}_5\text{H}_{11})\cdot\text{CHO}$, at 230° gives 25% of $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{C}_5\text{H}_{11}$ (III) and 75% of $\beta\text{-cyclohexylmethyl-n-heptyl alcohol}$ (IV), b.p. 158°/15 mm.

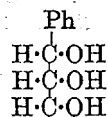
(*allophanate*, m.p. 108°), and at 130° 25% of (III) and 75% of a mixture of (IV) and the $\beta\text{-benzyl derivative}$.

R. S. C.

Arylglycerols. I. Preparation of two new forms of $\alpha\gamma\text{-diphenylglycerol}$. W. BRADLEY and J. K. EATON (J.C.S., 1938, 1578—1582; cf. Bigelow *et al.*, A., 1935, 346).—Two new forms of $\alpha\gamma\text{-diphenylglycerol}$, regarded as diastereoisomerides, are prepared. Bz_2O_2 and CHNaBz_2 in dry C_6H_6 at $<10^\circ$ afford $\omega\text{-benzoyloxy-}\omega\text{-benzoylacetophenone}$, m.p. 97°, reduced [H_2 (2 mols.), PtO_2 , EtOAc] to $\beta\text{-hydroxy-}\alpha\text{-benzoyloxy-}\beta\text{-phenylpropiofenone}$, m.p. 137°, and (after absorption of 5 H_2), to $\beta\text{-O-benzoyl-}\alpha\gamma\text{-diphenylglycerol}$ (I), m.p. 154.5—155.5°, CH_2Bz_2 , and BzOH . (I) is hydrolysed ($\text{KOH}\cdot\text{EtOH}$) to $\alpha\gamma\text{-diphenylglycerol}$, m.p. 117—118°, which is probably (II). Phenylstyrylcarbinol and BzO_2H in CHCl_3 at 0° for 24 hr. afford an oxide, hydrolysed by 0.02N-HCl to $\alpha\gamma\text{-diphenylglycerol}$, m.p. 128° [probably (III)] (*triacetate*, m.p. 129—130°). Neither new form shows tendency to hydration.



(II.)



Ph (III.)

The *cis*-form of $\alpha\text{-phenylglycerol}$, m.p. 99.5° (*tribenzoate*, m.p. 151—152°) (Prévost and Lossen, A., 1934, 649), is identical with that, m.p. 98—99°, obtained by Platt and Hibbert (A., 1933, 398) from $\alpha\text{-phenylglycidol}$.

A. T. P.

Oxidation of methylcholanthrene and 3:4-benzpyrene with lead tetra-acetate; further derivatives of 3:4-benzpyrene. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1938, 60, 2542—2548; cf. A., 1938, II, 406).— $\text{Pb}(\text{OAc})_4$ readily oxidises methylcholanthrene (I) at C_{15} , and, less readily, 3:4-benzpyrene (II). $\text{NPhMe}\cdot\text{CHO}$ introduces CHO into (II) at C_{15} . Susceptibility to attack by $\text{Pb}(\text{OAc})_4$, $\text{NPhMe}\cdot\text{CHO}$, and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ is correlated with carcinogenic activity, which may be due to hydroxylation of the active compound. Reaction with $\text{NPhMe}\cdot\text{CHO}$ is the least sp. of the reactions, but diazo-coupling tends to exaggerate differences. The reactivity of (I) at C_{15} is in line with that of Me at C_{10} , in 1:2-benzanthracene, the CH_2 being more reactive than Me. However, the distinguishing property of (I) and (II) is possession of an unusually reactive centre rather than of any sp. grouping.

$\text{Pb}(\text{OAc})_4$ in AcOH and (I) in C_6H_6 at 0° give 46% of 15-acetoxy- (III), m.p. 179.5—180.5° (decomp.), and 7% of 15-keto-20-methylcholanthrene (IV), m.p. 262—263°. Hydrolysis of (III) gives 15-hydroxy-20-methylcholanthrene, m.p. ~214—216° (decomp.), oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7\cdot\text{AcOH}$) to (IV), which is also similarly obtained in 13% yield directly from (I). The structure of (IV) etc. follows from its further oxidation ($\text{Na}_2\text{Cr}_2\text{O}_7$) to 6-methyl-1:2-benzanthraquinone-5-acetic acid [Me ester, m.p. 221.5—222° (lit., 213—214°)]. $\text{Pb}(\text{OAc})_4$ and (II) at room temp. give 85% of an *OAc*-derivative, m.p. 209.5—210°. Addition of 3:4-trimethylenebenzanthrone-7 to LiMe

in Et₂O and heating the product in C₆H₆ gives 21% of 6-methyl-3:4-trimethylenebenzanthrone-7, m.p. 220—220.5° [converted by distilling with Zn dust at 250 mm. into 6-methyl-3:4-benzpyrene, m.p. 171—171.5° [picrate, m.p. 181.5—182.5°; C₆H₃(NO₂)₃ additive compound, m.p. 209—210°], and an oil, which by distillation with Zn dust affords 2% of 5-methyl-3:4-benzpyrene (V), m.p. 215.7—216.2° [picrate, m.p. 207—208°; C₆H₃(NO₂)₃ additive compound, m.p. 230—231°]. NPhMe·CHO, (II), and POCl₃ in o-C₆H₄Cl₂ at 100° give 3:4-benzpyrene-5-aldehyde (90% yield), m.p. 202.5—203.5°, the hydrazone, m.p. 219.5—220.5° (decomp.), of which with NaOEt-EtOH at 210—215° gives (V). M.p. are corr. 4'-Methyl-3:4-benzpyrene and its 1':2'-H₂-derivative are carcinogenic. R. S. C.

Inversion in the pinacol rearrangement of 1:2-dimethylcyclopentane-1:2-diol. P. D. BARTLETT and A. BAVLEY (J. Amer. Chem. Soc., 1938, 60, 2416—2419).—1:2-Epoxy-1:2-dimethylcyclopentane (prep. from the olefine by BzO₂H in CHCl₃ in 85% yield), b.p. 120—122.5°/20 mm., with very dil. H₂SO₄ gives trans-1:2-dimethylcyclopentane-1:2-diol (I), m.p. 99.5—101° (corr.). The cis-diol (II), b.p. 142—146°/20 mm. [benzylidene ether, m.p. 120—122.5° (corr.)], is obtained from the cyclopentene and aq. COMe₂-KMnO₄. The configurations are proved by the fact that (II) reacts with Pb(OAc)₄ 1600 times as fast as does (I). With 20% (vol.) H₂SO₄ (II) gives 2:2-dimethylcyclopentanone (85% yield as semicarbazone); under similar conditions (I) gives only tars, which probably arise by dehydration and polymerisation, although attempts to "catch" the cyclopentene by Br, (:CH·CO)₂O, or p-O·C₆H₄·O failed. With 0.2N-H₂SO₄ (II) reacts much faster than does (I). Thus, in the pinacol rearrangement elimination of OH and arrival of the migrating radical occur on opposite sides of the same C atom (cf. A., 1937, II, 288). R. S. C.

Retardation in the oxidation of adrenaline.—See A., 1938, I, 628.

Di-(γ-chloro-α- or -β-hydroxypropyl)arylamines.—See B., 1938, 1268.

Hydrolysis of benzhydryl chloride in acetone.—See A., 1938, I, 627.

Spinastanol. Its identity with fucostanol and stigmastanol. C. D. LARSEN (J. Amer. Chem. Soc., 1938, 60, 2431—2434).—By quant. hydrolysis of the acetate and benzoate, by prep. of derivatives and of the ketone and its oxime, the dicarboxylic acid (I) and its Me₂ ester, and the hydrocarbon, and by comparison with authentic samples, spinastanol, m.p. 136.5—137°, is shown to be identical with fucostanol and stigmastanol and to differ (probably in the side-chain) from sitostanol and ostreastanol. Pure (I) has m.p. 236—237° (corr.). R. S. C.

Sterols. E. BURŠ and S. LISIOVÁ (III Kongr. slovenskih Aptekara, 1935, 213—220; Chem. Zentr., 1937, i, 2379).—Hyoscyamus-seed oil contains ~0.4% of a sterol (I), C₂₈H₄₈O, H₂O, m.p. 119—120° [benzoate, m.p. 123—124°; acetate (+H₂O), m.p. 124°, converted by Br-AcOH into a compound, C₃₀H₅₂O₃Br₆], which with PCl₅ gives a Cl-compound

(Cl 12.27%), m.p. 87—88°. Reduction (Na, C₅H₁₁·OH) of (I) affords the H₆-derivative, m.p. ~90°, which with Br-Et₂O-AcOH gives a compound (Br 13.92%), m.p. 57—58°. H. B.

Additive compounds of sterols. J. HADÁČEK and Z. ROSENBERG (Časopis českoslov. Lék., 1936, 16, 225—229; Chem. Zentr., 1937, i, 2379).—Wheat-germ oil contains a sterol (I), m.p. 136°; its digitonide can be obtained directly from the oil and EtOH-digitonin at 70°. Cholesterol, (I), and the phytosterol from apricot oil form additive compounds with saponin and cyclamin. H. B.

Phytosterol, C₂₇H₄₄O, H₂O, m.p. 132°, and substance, C₄₅H₆₆O₁₈, m.p. 100—102°, from Cape gooseberry fruit.—See A., 1938, III, 1066.

trans-Δ^{5:6}-Dehydrodeoxoandrosterone. Y. RAOUL and P. MEUNIER (Compt. rend., 1938, 207, 681—683).—Reduction (Clemmensen) of trans-Δ^{5:6}-dehydroandrosterone (I) or of the semicarbazone of its Ac derivative with NaOEt affords a product, which when freed from (I) by Girard and Sandulesco's reagent T (cf. A., 1936, 1397) in boiling AcOH-EtOH affords trans-Δ^{5:6}-dehydrodeoxoandrosterone (II), m.p. 104°, [α]_D²⁵ +21.3° [Ac derivative, m.p. 114°, hydrolysed to (II)]. (II) is a trans-alcohol since it gives a ppt. with digitonin. Its androgenic activity is $\frac{1}{100}$ of that of testosterone; its cestrogenic activity is almost nil. The substance prepared by De Fazi and Pirrone (A., 1937, II, 147) was not (II).

J. L. D.

Steroids and sex hormones. XLV. Hydrogenation of equilenin to non-phenolic products. L. RUZICKA, P. MÜLLER, and E. MÖRGELI (Helv. Chim. Acta, 1938, 21, 1394—1400).—Reduction of equilenin (I) with Na and boiling amyl alcohol gives 80% of non-phenolic products the chief of which is hexahydroequilenin, m.p. 181°, which does not give a colour with diazobenzenesulphonic acid. Catalytic hydrogenation (PtO₂ in EtOH containing HCl) of (I) leads after absorption of 3 mols. of H₂ to α-dihydroequilenin, m.p. 248°, and 17-hydroxy-Δ^{5:7:9}-œstratriene (II), m.p. 145°. Complete hydrogenation yields (II) and an isomeric hexahydroequilenin, m.p. 166.5° (diacetate, m.p. 115°). All m.p. are corr. The possibility of converting tetrahydroneergosterol into œstrone therefore appears slight (cf. Marker, A., 1938, II, 408). H. W.

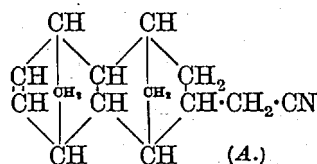
Sterols. XLV. Neutral reduction products of equilenin. R. E. MARKER, E. ROHRMANN, E. L. WITTLE, and F. H. TENDICK (J. Amer. Chem. Soc., 1938, 60, 2440—2442).—The neutral fraction, obtained from equilenin or α-dihydroequilenin by Na-C₅H₁₁·OH (A., 1938, II, 408), contains œstratriene-3(α):17(α)-diol (I), m.p. 172° (benzoate, m.p. 195°); that from β-dihydroequilenin contains Δ^{5:7:9}-œstratriene-3(α):17(β)-diol (II), m.p. 179°. With CrO₃ (I) and (II) give only oils. Remesov's compound (A., 1938, II, 18) is probably Δ^{5:7:9}-œstratriene-3(β)-ol-17-one. Configuration at C₁₃ in (I) and (II) is uncertain. R. S. C.

Mixed esters of œstradiol.—See B., 1938, 1364.

Androstane-3:5:6-triol-17-one and -3:5:6:17-tetraol. Aliphatic esters of oestra-diol.—See B., 1938, 1364.

Diene syntheses. VI. Diene syntheses with allyl compounds. K. ALDER and E. WINDEMUTH (Ber., 1938, 71, [B], 1939—1957).—The possibilities of a diene synthesis at a double linking which is not part of a conjugated system and is without special constitutive features of other types have been investigated further (cf. A., 1938, II, 131). $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$ and cyclopentadiene (I) at 175—180° give 2:5-*endomethylene*- Δ^3 -tetrahydrobenzyl alcohol, b.p. 92—95°/13 mm., the constitution of which is established by its hydrogenation (PtO_2 in EtOAc) to 2:5-*endomethylene*hexahydrobenzyl alcohol (II), b.p. 95—96°/13 mm. (H phthalate, m.p. 111—112°). Addition of (I) to $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$ and to $\text{CH}_2\text{:CH}\cdot\text{CHO}$ leads to compounds similar to one another in structure and configuration. Addition occurs the more rapidly with the aldehyde. Additivity of $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$ is not impaired by esterification. Thus allyl salicylate and (I) at 175—180° afford 2:5-*endomethylene*- Δ^3 -tetrahydrobenzyl salicylate, b.p. 185—186°/11 mm., which with PhN_3 gives the *hydrotriazole*, $\text{C}_{21}\text{H}_{21}\text{O}_3\text{N}_3$, m.p. 154°, and is hydrogenated to 2:5-*endomethylene*hexahydrobenzyl salicylate, b.p. 193°/14 mm., hydrolysed to (II). A less active diene component, anthracene (III), adds to $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$ in C_6H_6 at 210—220° giving 9:10-*endoethylene*-9:10-*dihydro*-9-*anthranylmethyl alcohol*, silky needles, m.p. 112°, or hard prisms, m.p. 105° (acetate, m.p. 122°). Crotyl alcohol and (I) at 170° give 6-methyl-2:5-*endomethylene*- Δ^3 -tetrahydrobenzyl alcohol, b.p. 100—115°/12 mm.; the corresponding acetate, b.p. 98—102°/vac., is hydrogenated (PtO_2 in EtOAc) to the acetate, b.p. 100—102°, of 6-methyl-2:5-*endomethylene*hexahydrobenzyl alcohol, b.p. 103—104°/12 mm. (H phthalate, m.p. 98°). Allyl halides behave similarly to allyl alcohol. Thus (I) and $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Cl}$ at 170—180° give 2:5-*endomethylene*- Δ^3 -tetrahydrobenzyl chloride, b.p. 54—57°/11 mm. (additive compound, $\text{C}_{14}\text{H}_{16}\text{N}_3\text{Cl}$, m.p. 133—134°, with PhN_3), hydrogenated to 2:5-*endomethylene*hexahydrobenzyl chloride, b.p. 69—70°/12 mm. $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Cl}$ and (III) afford 9:10-*endoethylene*-9:10-*dihydro*-9-*anthranylmethyl chloride*, m.p. 115—116°. $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Br}$ and (I) at 170° give 2:5-*endomethylene*- Δ^3 -tetrahydrobenzyl bromide, b.p. 75—77°/13 mm., whence 2:5-*endomethylene*hexahydrobenzyl bromide (IV), b.p. 83—84°/13 mm., which, like the chloride, is hydrolysed to (II). (I) and $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{I}$ at 100—105° give 2:5-*endomethylene*- Δ^3 -tetrahydrobenzyl iodide, b.p. 105—115°/15 mm. $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NH}_2$ and (I) at 170° give 2:5-*endomethylene*- Δ^3 -tetrahydrobenzylamine, b.p. 61—62°/12 mm., hydrogenated (PtO_2) to 2:5-*endomethylene*hexahydrobenzylamine (hydrochloride, m.p. >300°; corresponding *carbamide*, $\text{C}_9\text{H}_{16}\text{ON}_2$, m.p. 124°). The base is also obtained from (IV) and $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NK}$. $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and (I) at 175—180° yield 2:5-*endomethylene*- Δ^3 -tetrahydrophenylacetic acid, b.p. 137—139°/12 mm., hydrogenated (PtO_2 in EtOAc) to 2:5-*endomethylene*hexahydrophenylacetic acid (V), b.p. 141—142°/13 mm. (chloride, b.p. 94—95°/13 mm.,

whence the *anilide*, m.p. 138°, and the *amide*, m.p. 160°). $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CN}$ and (I) at 170—180° give 2:5-*endomethylene*- Δ^3 -tetrahydrophenylacetoneitrile



(VI), b.p. 89—93°/11 mm. (adduct, $\text{C}_{15}\text{H}_{16}\text{N}_4$, m.p. 174—175°, with PhN_3), and small amounts of the adduct (A), b.p. 165°/11 mm. (corresponding *hydrotriazole*, $\text{C}_{20}\text{H}_{22}\text{N}_4$, m.p. 202—203°). (VI) is hydrogenated (PtO_2 in EtOAc) to 2:5-*endomethylene*hexahydrophenylacetoneitrile, b.p. 103—105°/14 mm., which is hydrolysed to (V), also obtained from (IV) (or the chloride) by the Grignard method and degraded to the corresponding amine. $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NCS}$ and (I) at 145—155° yield 2:5-*endomethylene*- Δ^3 -tetrahydrobenzylthiocarbimide, b.p. 120—123°/12 mm. (corresponding *hydrotriazole*, m.p. 116—117°). $\beta\gamma$ -Dimethylbutadiene and $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NCS}$ give an adduct, b.p. 137—138°/12 mm. Eugenol and (I) at 170—180° afford 2-*methoxy*-4-2':5'-*endomethylene*- Δ^3 -tetrahydrobenzylphenol, b.p. 138—143°/0.1 mm., m.p. 35° (corresponding *hydrotriazole*, $\text{C}_{21}\text{H}_{23}\text{O}_2\text{N}_3$, m.p. 210—211°). The steric course of the diene synthesis with allyl compounds is discussed.

H. W.

New diene syntheses. III. E. LEHMANN (Ber., 1938, 71, [B], 1869—1874; cf. A., 1936, 605).—2:4:1':2'-Tetramethyl- Δ^5 -tetrahydrodiphenyl (I) [incorrectly described (*loc. cit.*) as the 1:3:1':2'-Me₄ compound] is dehydrogenated by Se at 315—320° to 2:4:2':3'-tetramethyldiphenyl, b.p. 162—163°/12 mm., which is oxidised to the *diphenyltetra-carboxylic acid*, m.p. 255—256°. Rearrangement occurs during dehydrogenation so that no evidence is thereby afforded with regard to the constitution of (I) and allied compounds (*loc. cit.*). The cyanohydrin from the NaHSO_3 compound of 2-phenyl-2-methyl- Δ^3 -tetrahydrobenzaldehyde and aq. KCN is hydrolysed (cold Et_2O -conc. HCl) to 2-phenyl-2-methyl- Δ^3 -tetrahydromandelamide, forms, m.p. 200.5° and 182°, which is converted by KOH-EtOH into 2-phenyl-2-methyl- Δ^3 -tetrahydromandelic acid, forms, m.p. 180—181° (II) and 183—184°, respectively. (II) is hydrogenated (Pd-BaSO₄ in EtOAc) to 2-phenyl-2-methylhexahydromandelic acid, m.p. 172—173°. 2-p-Tolyl-2-methyl- Δ^3 -tetrahydrobenzaldehyde is converted into the non-cryst. cyanohydrin (III) and thence into 2-p-tolyl-2-methyl- Δ^3 -tetrahydromandelamide, forms, m.p. 202° and 167°, whence the corresponding *acids*, m.p. 169—170° (IV) and 181°, respectively. Hydrogenation (Pd-BaSO₄ in EtOAc) of (IV) affords 2-p-tolyl-2-methylhexahydromandelic acid, m.p. 180—180.5°, which is isomerised by conc. HI at 115—120° to an *acid*, m.p. 185—186°. Reductive hydrolysis (75% HI at 140—150°) of (III) gives mainly a *hydrocarbon*, $\text{C}_{16}\text{H}_{22}$ or $\text{C}_{15}\text{H}_{20}$, b.p. 136—137°/12 mm., accompanied by an *acid*, $\text{C}_{16}\text{H}_{16}\text{O}_2$, m.p. 151°.

H. W.

Isotopic exchange reactions of organic compounds. IV. Mechanism of racemisation of phenyl-p-tolylacetic acid. D. J. G. IVES and G. C. WILKS (J.C.S., 1938, 1455—1458).—The rate of racemisation of optically active phenyl-p-tolyl-

deuteroacetic acid in 0.2N. aq. solution at 100° in presence of 10% excess of NaOH in Ag vessels = rate of loss of D (velocity coeffs. = 0.0050 hr.⁻¹). Since the latter rate = rate of ionisation of the α -D, the racemisation proceeds by an ionisation mechanism; the same mechanism is considered to hold for the racemisation of phenyl-*p*-tolylacetic acid. The velocity coeff. for the rate of racemisation of this acid under the same conditions but in a solvent containing 3% of D₂O is 0.023 hr.⁻¹, the coeff. for the accompanying exchange reaction being 0.0077 hr.⁻¹; these data are shown to be compatible with the proposed mechanism. Under the conditions of experiment H ionises 4.5 times as fast as D. H. G. M.

Separation of tyrosine, thyroxine, 3:5-diiodotyrosine, and peptides containing the tyrosine residue. S. J. VON PRZYŁĘCKI and R. TRUSZKOWSKI (Biochem. Z., 1938, 298, 326—327).—When a mixture containing the above compounds is freed from other material by extraction with Pr⁺CO₂H and then shaken with AcOH tyrosine and thyroxine, but not the other substances, remain undissolved. Tyrosine is separated from thyroxine by dissolution in 0.1N-HCl. W. McC.

Alicyclic amino-acids. J. P. GREENSTEIN and J. WYMAN, jun. (J. Amer. Chem. Soc., 1938, 60, 2341—2347).—4-Aminocyclohexane-1-carboxylic acid (+0.5H₂O), obtained by reduction (H₂, PtO₂) of *p*-NH₂·C₆H₄·CO₂H in respectively aq. suspension or N-HCl, has m.p. 260° (1a) or 285° (1b). Similarly, *m*-NH₂·C₆H₄·CO₂H gives 3-aminocyclohexane-1-carboxylic acid (+0.5 H₂O), m.p. 278° (IIa) or 264° (11b). *o*-NH₂·C₆H₄·CO₂H could not be reduced catalytically. Identical dielectric increments are shown by (1a) and (1b) and by (IIa) and (11b); differences in m.p. are probably not significant. Comparison of the dielectric consts. of (1a), (1b), (IIa), (11b), and the 2-isomeride with those of aliphatic NH₂-acids indicates approx. the same freedom of rotation in both series. R. S. C.

Synthesis of phenanthrene and hydrophenanthrene derivatives. VIII. Substances related to degradation products of morphine. L. F. FIESER and H. L. HOLMES (J. Amer. Chem. Soc., 1938, 60, 2548—2555; cf. A., 1937, II, 105).—Reduced phenanthrene derivatives, which are substituted at C₍₁₃₎, are synthesised as first steps in the synthesis of morphine degradation products. Stereoisomerism at C₍₁₃₎ was not encountered. 4:5:2:1-(OMe)₂C₆H₂Br·[CH₂]₃·CO₂H (modified prep. in 83% yield), m.p. 137.8—138.8° (lit., 135—136°), gives the Et ester, m.p. 49.5—50.5°, the structure of which is proved by oxidation (KMnO₄) to 4:5:2:1-(OMe)₂C₆H₂Br·CO₂H, and which with Et₂C₂O₄ and NaOEt gives Et₂ α -oxalyl- γ -2-bromo-4:5-dimethoxyphenylbutyrate, m.p. 74.7—75.3°. With hot 18% H₂SO₄ this gives 90% of α -keto- δ -2-bromo-4:5-dimethoxyphenylvaleric acid, m.p. 93—94° (Et ester, b.p. 225—227°/9 mm.; enol acetate, m.p. 148.4—149°), cyclised by 70% H₂SO₄ at 80° to 5-bromo-7:8-dimethoxy-3:4-dihydro-1-naphthoic acid (I) (55%), m.p. 172—173° [Me ester (II), m.p. 76—77°, b.p. 174—175°/2 mm.]. H₂-PtO₂ in EtOH reduces (I) to 5-bromo-7:8-dimethoxy-1:2:3:4-tetrahydro-1-

naphthoic acid, m.p. 147—148°, which is debrominated by H₂-PdO₂ in EtOH, yielding 7:8-dimethoxy-1:2:3:4-tetrahydro-1-naphthoic acid, m.p. 119.5—120°. With (CH₂:CMe)₂ at 175—185° (II) gives 54% of Me 1-bromo-3:4-dimethoxy-6:7-dimethyl-5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylate, m.p. 154—155°, resistant to hydrogenation. However, with (CH₂:CH)₂, best at 220—230°, (II) gives only 8—9% of Me 1-bromo-3:4-dimethoxy-5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylate (III), m.p. 105—106°, hydrogenated (PtO₂) in AcOH readily to the 5:6:7:8:9:10:13:14-H₈-ester, m.p. 112.5—113.5°, debrominated by H₂-Pd-BaSO₄ in AcOH to Me 3:4-dimethoxy-5:6:7:8:9:10:13:14-octahydrophenanthrene-13-carboxylate, m.p. 142.8—143.2°, from which the corresponding acid (IV), m.p. 202.4—203.4°, is obtained in 39% yield by NaOEt-EtOH at 175—185°. (CH₂:CH)₂ adds to (I) in C₆H₆ at 185—195° to give 18% of 1-bromo-3:4-dimethoxy-5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylic acid, m.p. 260—261° (decomp.) [Me ester = (III)], hydrogenated successively to the 5:6:7:8:9:10:13:14-H₈-acid, m.p. 233—234°, and (IV). Prep. of Et 5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylate, b.p. 197—198°/14 mm., its 6:7-Me₂, b.p. 197—198°/14 mm., and 3-OMe-derivative, b.p. 212—215°/17 mm., is improved. 5:6:7:8:9:10:13:14-Octahydrophenanthrene-13-carboxylic acid, m.p. 144—145°, its Et ester, b.p. 180—181°/16 mm., and its 3-OMe-derivative, m.p. 174.5—175.5°, are prepared by hydrogenating the corresponding H₂-compounds. 3-Methoxyphenanthrene is obtained from 3-methoxy-5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylic acid by Se at 300—320°. A diene reaction with (CH₂:CMe)₂ at 120—160° gives 85% of Et 3-methoxy-6:7-dimethyl-5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylate, m.p. 67—68°, b.p. 197—199°/5 mm., hydrolysed by NaOEt at 170° to the corresponding acid, m.p. 164—165° (chloride, b.p. 215°/15 mm.), which is hydrogenated to 3-methoxy-6:7-dimethyl-5:6:7:8:9:10:13:14-octahydrophenanthrene-13-carboxylic acid, m.p. 204—206°, and converted by Se into 3-methoxy-6:7-dimethylphenanthrene, m.p. 119—120° (picrate, m.p. 160—162°). Na-iso-C₅H₁₁·OH (not Na-EtOH) reduces the hexa- and octa-hydrophenanthrene-13-carboxylates to the 13-OH·CH₂ derivatives, usually in 70—80% yield, small amounts of the acid being recovered. Thus are obtained 6:7-dimethyl- (V), m.p. 73—74° [acetate (VI), b.p. 176—177°/5 mm.], 3-methoxy-, m.p. 122.4—122.8°, and 3-methoxy-6:7-dimethyl-, m.p. 66—67°, -13-hydroxymethyl-5:8:9:10:13:14-hexahydrophenanthrene, 13-hydroxymethyl-5:6:7:8:9:10:13:14-octahydrophenanthrene, m.p. 48.8—49.5° (acetate, b.p. 136—138°/3 mm.), 6:7-dimethyl-, m.p. 68—69°, b.p. 203—205°/15 mm. [also obtained by hydrogenating (V); acetate, b.p. 210—212°/15 mm.], and 3-methoxy-6:7-dimethyl-13-hydroxymethyl-5:6:7:8:9:10:13:14-octahydrophenanthrene, m.p. 76.7—77.9°. 6:7-Dimethyl-5:6:7:8:9:10:13:14-octahydrophenanthrene-13-carboxylic acid melts at 189—191° after softening. With PCl₅ in C₆H₆ (VI) gives 65% of 6:7-dimethyl-13-chloromethyl-

5 : 8 : 9 : 10 : 13 : 14-hexahydrophenanthrene (VII), b.p. 196—198°/3 mm. (could not be converted into the 13-CN·CH₂ compound), hydrogenated (PtO₂) in AcOH to an oily mixture, which with Se gives 2 : 3-dimethylphenanthrene, thus proving that chlorination occurs without migration of the CH₂Cl. Se-dehydrogenation of (V) or (VII) gives a (?) trimethylphenanthrene, m.p. 148—149°. M.p. are corr. R. S. C.

Esterification of benzoic acid with methyl alcohol using isotopic oxygen.—See A., 1938, I, 627.

Reactions of sodium and potassium on acid chlorides. I. A. PEARL, T. W. EVANS, and W. M. DEHN (J. Amer. Chem. Soc., 1938, 60, 2478—2480).—NPh₂·COCl (I) and Na in boiling PhMe react thus: (I) + 2Na → NPh₂·CNaCl·ONa → NPh₂Na + CO + NaCl; NPh₂Na + (I) → NaCl + CO(NPh₂)₂. When an excess of Na is used, some NPh₂Na can be isolated. (CO·NPh₂)₂ is not formed (cf. A., 1930, 1427) and is not an intermediate as it is unchanged by heating with Na in boiling PhMe or alone at 195°. In dry xylene BzCl and Na or K give NaCl (or KCl) and Bz₂O, atm. O₂ being absorbed during the reaction. *o*-C₆H₄(COCl)₂ and (·CH₂·COCl)₂ give 70 and 60% yields, respectively, of the anhydrides. *p*-C₆H₄Me·SO₂Cl and K in dry xylene give KCl and (*p*-C₆H₄Me·SO₂)₂. BzCl and Na in Et₂O give EtOBz. R. S. C.

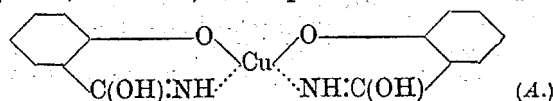
Degradation of dibenzoyl disulphide. E. S. COOK and K. BAMBACH (J. Amer. Pharm. Assoc., 1938, 27, 758—760).—Bz₂S₂ gives low yields of BzOH on oxidation with alkaline KMnO₄ or conversion into NHPhBz followed by acid hydrolysis. Quant. conversion into BzOH is effected by boiling with 40% (wt./vol.) aq. KOH (cf. Shelton and Rider, A., 1936, 1106). F. O. H.

Quantitative aspects of asymmetric transformation. M. M. JAMISON and E. E. TURNER (J.C.S., 1938, 1646—1662; cf. A., 1930, 1287; 1938, II, 59).—If an optically active, optically stable base (I), *d*-R₃N, and an equiv. of an optically unstable acid (II), *dl*-HA, are dissolved in a solvent, the two diastereoisomerides are formed in equal amounts at the moment of mixing, but can undergo interconversion, and optical rotation will correspond with the equilibrium: *d*-R₃N, *d*-HA ⇌ *d*R₃N, *l*-HA ("first-order asymmetric transformation"). When one salt crystallises out (complete conversion) and none of the other form appears, it is termed "second-order transformation" (Kuhn, A., 1932, 269). Vals. of α plotted against ratio of (I) : (II) gives "addition curves" of two types, viz., (a) where addition of excess of (II) has no marked effect on α; such acids are stereochemically of four types, viz., (i) the configurationally symmetrical acids, e.g., *o*-C₆H₄Me·CO₂H, *o*-OH·C₆H₄·CO₂H, and 2 : 4-dinitrodiphenyl-6-carboxylic acid (III); (ii) the non-resolvable 3'-Me derivative of (III); (iii) the resolvable, optically stable 2'-Me derivative of (III); (iv) *N*-benzoyldiphenylamine-4-carboxylic acid and its 4'-Cl-derivative; (b) where (II) in excess of 1 equiv. gives a relatively large change in α, e.g., *N*-benzoyldiphenylamine-2-carboxylic acid (IV) and its 2' : 4'-Cl₂- (V) and -Me₂ (VI) derivatives. Addition curves for (VI) and nor-

d-*ψ*-epedrine show that excess of (VI) has a marked effect in non-hydroxylic solvents (high or low dielectric consts.), but no change in α is observed in MeOH or EtOH (mechanisms discussed). Inferred "first-order asymmetric transformation" has been shown by observing change of α with (V) or (VI) and nor-*d*-*ψ*-epedrine in CHCl₃ at -31° (-30°) (cf. Mills and Clark, A., 1936, 492); rapid mutarotation occurs [not observed with (IV)]. Activation of (V) and (VI) is stated to be due to restricted rotation within the mol. and the manner of operation is discussed. With *N*-benzoyl-4 : 6 : 4'-tribromodiphenylamine-2-carboxylic acid (VII), nor-*d*-*ψ*-epedrine in CHCl₃ at room temp. produces excess of a *d*-activation product, whereas cinchonidine (VIII) affords excess of *l*- ("first order"). From a warm COMe₂ solution of (VII) and 1 equiv. of (VIII), the optically pure cinchonidine *d*-salt of (VII) separates. The cinchonidine salts are resolved in COMe₂ at -15°. Decomp. of the *d*- and *l*- (impure) -salts in C₅H₅N at -15° by HCl-ice affords the respective *d*- and *l*-forms of (VII); the rates of racemisation of the acids in EtOH are determined. Examination of the kinetics of the first-order asymmetric transformation of salts of (VII) shows that when acid is > that equiv. to base, not only do the relative proportions of the two diastereoisomerides change, but also one form of the free acid is formed in slight excess. Effect of excess of acid on salt dissociation is probably small. The supposition, hitherto, that the diastereoisomerides alone contribute to total rotation at equilibrium, is true only if the salts are completely undissociated. A. T. P.

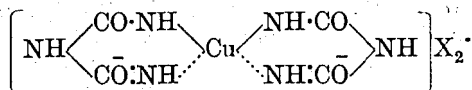
Hydrolysis of higher homologues of acetylsalicylic acid. A. LESPAGNOL and (MLLE.) BAR (Bull. Soc. chim., 1938, [v], 5, 1360—1365).—Et *o*-allyloxybenzoate, b.p. 153°/13 mm., is converted at 230° for 1 hr. into Et 3-allylsalicylate, b.p. 270—278°, hydrolysed by MeOH-KOH to the acid, m.p. 96°, which with Ac₂O-KOAc gives 2-acetoxy-3-allylbenzoic acid, m.p. 94° (cf. Claisen, A., 1912, i, 965). 2-Acetoxy-6-methyl-3-isopropylbenzoic acid is obtained from *o*-thymotic acid (cf. Spallino, A., 1910, i, 38). 5 : 2 : 1-C₆H₃MeBu^γ·OH with CO₂ and Na (added gradually) in boiling xylene affords 2-hydroxy-6-methyl-3-tert.-butylbenzoic acid, m.p. 170° (2-acetoxy-derivative, m.p. 108°). The introduction of groups, viz., Me < allyl < Pr^β < Bu^γ, into the 3-position of acetylsalicylic acid, diminishes the rate of hydrolysis, probably due to steric hindrance. A. T. P.

Theory of the biuret reaction. I. Internally complex salts of hydroxylated acid amides. P. PFEIFFER and H. GLASER (J. pr. Chem., 1938, [ii], 151, 145—159).—Complex Cu salts of type (A)



are obtained from the requisite *o*-hydroxy-acid amide in MeOH or dil. aq. alkali with MeOH-Cu tetrammine acetate or aq. Cu(OAc)₂ respectively. Thus are obtained *Cu salicylamide* (I), *salicylmethylamide* (II), *salicylanilide* (III), 3 : 5-dibromosalicylamide (IV), decomp. ~217—218° (also + 4NH₃), *β*-resorcylamide,

2-hydroxy-4-methoxybenzamide (anhyd. and $+2\text{H}_2\text{O}$) (V), *acetoacetamide* (VI) (also $+4\text{C}_5\text{H}_5\text{N}$), and *benzoyl-acetamide* (VII) ($+4\text{C}_5\text{H}_5\text{N}$ and $+0.75\text{C}_5\text{H}_5\text{N}$). The salts are green to brown in colour and are decomposed by protracted heating of their solutions in MeOH or $\text{C}_5\text{H}_5\text{N}$. With MeOH-KOH or MeOH-NaOH they usually give blue-violet solutions, only (II) and (III) being immediately decomposed with separation of $\text{Cu}(\text{OH})_2$. The Na_2 ($+2\text{H}_2\text{O}$) salt of (I), the K_2 salt of (IV), and the K_2 ($+4\text{H}_2\text{O}$) salt of (V) have been obtained cryst. On exposure to atm. moisture and CO_2 they are gradually decomposed particularly when moist with EtOH. They are immediately hydrolysed by H_2O with pptn. of $\text{Cu}(\text{OH})_2$. (VI) and (VII) give respectively blue and greenish-blue alkali salts which could not be obtained pure. To the red biuret-Cu-alkali salts the formula



may be ascribed. This can be extended to the analogous complex salts of $\text{CH}_2(\text{CO} \cdot \text{NH}_2)_2$ and $(\text{CO} \cdot \text{NH}_2)_2$, and to the polypeptides and proteins. β -Resorcylamide and 2-hydroxy-4-methoxybenzamide have m.p. 222—223° and 158°, respectively.

H. W.

Existence of complex sulphosalicylates. G. SPACU and C. G. MACAROVICI (Bul. Soc. Ştiinţe Cluj, 1936, 8, 364—375; Chem. Zentr., 1937, i, 68).—Treatment of Na sulphosalicylate with CuSO_4 affords the light green cryst. complex $\text{Na}_4[\text{CuR}_2] \cdot 7\text{H}_2\text{O}$ [$\text{R} = \cdot\text{O} \cdot \text{C}_6\text{H}_3(\text{CO}_2')(\text{SO}_3')$], in which the Cu is co-ordinately bound. Double decomp. with metal salts yields the complexes $[\text{Co en}_2\text{Cl}_2]_4[\text{CuR}_2]_6 \cdot 6\text{H}_2\text{O}$; $[\text{Co}(\text{NH}_3)_5\text{Cl}]_2[\text{CuR}_2]_4 \cdot 4\text{H}_2\text{O}$; $[\text{Co}(\text{NH}_3)_5\text{SCN}]_2[\text{CuR}_2]_4 \cdot 4\text{H}_2\text{O}$; $[\text{Co}(\text{NH}_3)_5\text{NO}_2]_2[\text{CuR}_2]_2 \cdot 2\text{H}_2\text{O}$; $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_4]_2[\text{CuR}_2]_4 \cdot 4\text{H}_2\text{O}$ (I); $[\text{Cd}(\text{H}_2\text{O})_6]_2[\text{CuR}_2]_2$; $\text{Ba}_2[\text{CuR}_2] \cdot 7\text{H}_2\text{O}$ (II); $\text{Pb}_2[\text{CuR}_2] \cdot 3\text{H}_2\text{O}$ (III); $[\text{Co en}_2\text{Cl}_2]\text{R}' \cdot \text{H}_2\text{O}$ [$\text{R}' = \text{OH} \cdot \text{C}_6\text{H}_3(\text{CO}_2')(\text{SO}_3')$]; $[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]\text{R}' \cdot \text{H}_2\text{O}$; $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_3(\text{H}_2\text{O})]\text{R}'$; $[\text{Co}(\text{C}_5\text{H}_5\text{N})_3(\text{H}_2\text{O})]\text{R}'$. (I) and (II) are prepared in presence of $\text{C}_5\text{H}_5\text{N}$; (III) is decomposed by $\text{C}_5\text{H}_5\text{N}$. The complex $[\text{Co en}_2\text{Cl}_2][\text{SO}_3 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO}_2\text{H}] \cdot \text{H}_2\text{O}$ is also described.

A. H. C.

Replacement of halogen in cyclic compounds by the cyano-group.—See B., 1938, 1270.

4-Nitro-*o*-tolunitrile. C. CANDEA and E. MACOVSKI (Bull. Soc. chim., 1938, [v], 5, 1350—1357).—*o*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{CN}$ and HNO_3 (d 1.535) at 20—50° for $\frac{1}{2}$ hr., or H_2SO_4 — HNO_3 (d 1.4) at 15—20°, afford 4:1:2- $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CN}$ (I), m.p. 106—108°, converted by H_2SO_4 — HNO_3 (d 1.52) at 100° into 3:5:2:1- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2\text{H}$ (II) and by *m*- $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ and piperidine at 160° for 20 min. into 4-nitro-2-cyano-3'-methoxystilbene, m.p. 145°. (I) is reduced (Zn, CaCl_2 , EtOH) to the 4- NH_2 -derivative (III), new m.p. 92° (*Bz* derivative, m.p. 174°) (cf. Landsberger, A., 1898, i, 210), and (?) 3:3'-dicyano-4:4'-dimethylhydrazobenzene, m.p. 188°. (III) and CS_2 in EtOH-KOH give *s*-di-2-cyano-*p*-tolylthiocarbamide, m.p. 182°. (I) and (II), but not (III), give colours with aq. KOH in COMe_2 (Janovsky reaction).

A. T. P.

Preparation of depsides of means of azides. II. Action of trimethylgalloyl azide on phenol and mononitrophenols. R. O. PEPE (Anal. Assoc. Quim. Argentina, 1938, 26, 51—56; cf. A., 1930, 1039).—3:4:5-(OMe) $_3\text{C}_6\text{H}_2 \cdot \text{CON}_3$ in COMe_2 reacts with the appropriate phenol in *N*-NaOH giving *o*-, m.p. 141°, *m*-, m.p. 144°, and *p*-, m.p. 175°, -nitrophenyl 3:4:5-trimethoxybenzoate in 35, 60, and 63% yields respectively.

F. R. G.

Electrometric titration of tannic acids.—See A., 1938, I, 625.

Strainless monocyclic rings. II. Synthesis of 3-methylcyclohexane-1-carboxylic-1-acetic acid and separation of its isomerides. M. QUDRAT-I-KHUDA, A. MUKHERJI, and (in part) P. BANERJI (J. Indian Chem. Soc., 1938, 15, 462—470; cf. A., 1931, 1055; Desai *et al.*, 1936, 846).—Et 3-methylcyclohexylidenecyanoacetate and KCN-EtOH give a product hydrolysed by conc. HCl (36 hr.) to 3-methylcyclohexane-1-carboxylic-1-acetic acid, separated through the NH_4 salt into four isomerides, viz., A, m.p. 88° (anhydride, b.p. 207°/35 mm.; imide, m.p. 138—139°; anilic acid, m.p. 166°; phenylimide, m.p. 100°; *p*-toluidinic acid, m.p. 172°; *p*-tolylimide, m.p. 78°), B, m.p. 99° [anhydride, m.p. 45°, b.p. 152—153°/10 mm.; imide, m.p. 91°; anilic acid, m.p. 170° (? 180°); phenylimide, m.p. 115°; *p*-toluidinic acid, m.p. 172°; *p*-tolylimide, m.p. 98°; β -naphthylamic acid, m.p. 182°; β -naphthylimide, m.p. 118°], C, m.p. 168° (anhydride, b.p. 159°/9 mm.; imide, m.p. 183°; anilic acid, m.p. 173°; phenylimide, m.p. 136°; *p*-toluidinic acid, m.p. 182°; *p*-tolylimide, m.p. 141°; β -naphthylamic acid, m.p. 191°; β -naphthylimide, m.p. 189°), and D, m.p. 157° (anhydride, m.p. 66°, b.p. 232°/55 mm.; imide, m.p. 176—177°; anilic acid, m.p. 171°). C is insol. in boiling C_6H_6 , D is extremely sol. in the cold, and A is more sol. in cold C_6H_6 than B. The % A + B rises if hydrolysis is prolonged, e.g., 46—50 hr. The anhydride of A and hot H_2O afford some B and D.

A. T. P.

Stereoisomerism of 1-carboxymethylcyclohexane-1-acetic acids. R. D. DESAI and R. F. HUNTER (Chem. and Ind., 1938, 1059—1060).—The 3-methylcyclohexane-1-carboxylic-1-acetic acid, m.p. 88°, of Qudrat-i-Khuda (*supra*) is a mixture of the forms, m.p. 108° and 163° (A., 1936, 846).

R. S. C.

Diene synthesis. VII. Partly hydrogenated phthalic and benzoic acids. Synthesis of 9:10-dicarboxylic acids of partly and completely hydrogenated naphthalene. K. ALDER and K. H. BACKENDORF (Ber., 1938, 71, [B], 2199—2209).—Crude $(\text{C} \cdot \text{CO}_2\text{H})_2$, as obtained by withdrawal of HBr from $(\text{CHBr} \cdot \text{CO}_2\text{H})$, and butadiene in dioxan at 170—180° give mainly $\Delta^{1:4}$ -dihydrophthalic anhydride (I), new m.p. 147° [corresponding acid, m.p. 152° (decomp.)], which does not add maleic anhydride; it is smoothly hydrogenated (Pd- CaCO_3 in EtOAc) to Δ^1 -tetrahydrophthalic anhydride (II), m.p. 74°, converted by warm aq. Na_2CO_3 and subsequent acidification into Δ^1 -tetrahydrophthalic acid, m.p. 126° (lit., m.p. 120°). As by-products of (I) there are isolated $\Delta^{1:4}$ -dihydrobenzoic acid, m.p. 123°, which reduces alkaline KMnO_4 and is hydrogenated to hexa-

hydrobenzoic acid (corresponding amide, m.p. 184°), and *cis*- $\Delta^{2:6}$ -*hexahydronaphthalene*-9:10-dicarboxylic acid (III), m.p. 226° [anhydride (IV), m.p. 102—103°; Me_2 ester (V), m.p. 100°], which is strongly unsaturated towards alkaline $KMnO_4$. (IV) is very readily hydrogenated (PtO_2) to *cis*-*decahydronaphthalene*-9:10-dicarboxylic anhydride (VI), m.p. 95—96° [corresponding acid, m.p. 202—203° (decomp.)]. Attempted dehydrogenation of (III) by Se at 350° gives a greatly decomposed product from which a little *o*- $C_6H_4(CO)_2O$ and $C_{10}H_8$ are extracted. The attempted isomerisation of (V) by $NaOMe$ to the *trans*-form was unsuccessful. (IV) is also obtained by the action of butadiene on (I) in dioxan at 170—180°. Butadiene, (II), and a little quinol in C_6H_6 at 170—180° give Δ^2 -*octahydronaphthalene*-9:10-dicarboxylic acid, m.p. 203° (decomp.); the corresponding anhydride, m.p. 67—68°, is reduced (PtO_2 in $AcOH$) smoothly to (VI). 3:6-*endo*Methylene- Δ^1 -tetrahydrophthalic anhydride and butadiene in ligroin at 170—180° afford 5:8-*endomethylene*-*cis*- Δ^2 -*octahydronaphthalene*-9:10-dicarboxylic anhydride, m.p. 142°, hydrogenated ($Pd-CaCO_3$ in $EtOAc$) to 5:8-*endomethylenecis*-*decahydronaphthalene*-9:10-dicarboxylic anhydride, m.p. 100—102°.

II. W.

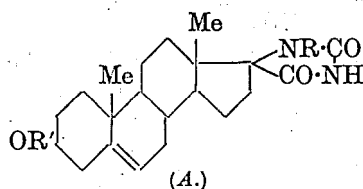
Separation and identification of amines with 3-nitrophthalic anhydride. J. W. ALEXANDER and S. M. MOELVAIN (J. Amer. Chem. Soc., 1938, 60, 2285—2287).—Primary and *sec.* amines with 3:1:2- $NO_2 \cdot C_6H_3(CO)_2O$ (I) in hot CCl_4 give nitrophthalimides and 2-nitro-6-carboxybenzamides, respectively, whilst *tert.* amines do not react. The imides are converted into phthalamic acids by 5% aq. $NaOH$ at room temp., and thence into the original amines rapidly by warm 10% HCl . The procedure for separating a mixture of amines is detailed. The structure of 2:6:1- $NO_2 \cdot C_6H_3(CO_2H) \cdot CO \cdot NH_2$, obtained from (I) and NH_3 , is confirmed by conversion into 3:2:1- $NO_2 \cdot C_6H_3(NH_2) \cdot CO_2H$ and thence into *m*- $NO_2 \cdot C_6H_4 \cdot CO_2H$. The following are new. 3-Nitro-*N*-isomyl-, m.p. 89—90°, -*m*-, m.p. 186—187°, and -*p*-bromophenyl-, m.p. 201—202°, -*o*-, m.p. 135—136°, -*m*-, m.p. 171—173°, and -*p*-chlorophenyl-, m.p. 198—199°, -*o*-, m.p. 163—164°, and -*p*-phenetyl-, m.p. 172—173°, -*o*-, m.p. 184—186°, -*m*-, m.p. 157—158°, and -*p*-anisyl-, m.p. 196—197°, - α -, m.p. 222—223°, and - β -naphthyl-phthalimide, m.p. 211—212°; 6-nitro-2-carboxybenz-*N*-benzyl-, m.p. 211—212°, -*butyl*-, m.p. 204—206°, -*ethyl*-, m.p. 203—204°, -*methyl*-, m.p. 192—194°, and -*propyl*-anilide, m.p. 222—225°. R. S. C.

Union of aryl nuclei. IV. Phenylphthalic acids and some derivatives. E. C. BUTTERWORTH, I. M. HEILBRON, D. H. HEY, and R. WILKINSON (J.C.S., 1938, 1386—1389).—Diazotised Me_2 4-aminophthalate (I) with C_6H_6 and aq. $NaOH$ gives a crude oil, hydrolysed to 4-phenylphthalic acid (Me_2 ester, m.p. 62—63°; imide, m.p. 200°), also obtained (after hydrolysis) from PhN_2Cl and *o*- $C_6H_4(CO_2Et)_2$ (II) in presence of alkali, and from $NPhAc \cdot NO$ and (II) at room temp. (stirring; 24 hr.). By similar methods diazotised (I) with $PhOMe$ gives a mixture of 4-*o*- and -*p*-anisylphthalic acids, m.p. 145—155°, and with $PhCl$ gives a mixture of 4-*o*- and -*p*-chlorophenylphthalic acids, m.p. 140—150°. Similarly, diazotised

Me_2 3-aminophthalate and $C_6H_6 \cdot NaOH$ give Me_2 3-phenylphthalate, m.p. 94°, hydrolysed to the acid, m.p. 181°, which when heated with conc. H_2SO_4 (40—50°; 10 min.) gives fluorenone-1-carboxylic acid. 4-Phenylphthalic anhydride (III) with $AlCl_3 \cdot C_6H_6$ gives a mixture of 4- and 5-phenylbenzophenone-2-carboxylic acids, m.p. 177—207°, which with anhyd. $ZnCl_2$ at 230°/2 hr. gives 2-phenylanthraquinone. With fuming HNO_3 and $AcOH$, (III) gives 4-*p*-nitrophenylphthalic acid, m.p. 178—179° (anhydride, m.p. 136—137°), which with $CrO_3 \cdot AcOH$ gives *p*- $NO_2 \cdot C_6H_4 \cdot CO_2H$. H. G. M.

Arylamides of aromatic dicarboxylic acids.—See B., 1938, 1269.

Addition of side-chains to *t*-dehydroandrosterone. K. MIESCHER and A. WETTSTEIN (Helv. Chim. Acta, 1938, 21, 1317—1326).—*t*(= *trans*)-Dehydroandrosterone acetate, KCN , $(NH_4)_2CO_3$, and



60% $EtOH$ under compressed CO_2 at 120° yield Δ^5 -3-*t*-acetoxy χ tiocolene-17-spirohydantoin (I) (A ; $R = H$; $R' = Ac$), m.p. 311° (decomp.), or under more drastic conditions Δ^5 -3-*t*-hydroxy χ tiocolene-17-spirohydantoin (A ; $R = R' = H$), decomp. >400° according to the rate of heating, also obtained by hydrolysing (I) with $KOH \cdot Pr^aOH$ and from *t*-dehydroandrosterone (II), KCN , $(NH_4)_2CO_3$, and CO_2 in 70% $EtOH$ at 135°, and converted by $Ac_2O \cdot KOAc$ at 125° into Δ^5 -3-*t*-acetoxy χ tiocolene-17-spiro-1'-acetylhydantoin (A ; $R = R' = Ac$), decomp. about 330°. (II) is transformed by $HClN$ followed by $Ac_2O \cdot C_5H_5N$ into *t*-dehydroandrosteronecyanohydrin diacetate (III), m.p. 215—217°, converted by the protracted action of $HCl \cdot EtOH$ in $CHCl_3$ at 2° into Δ^5 -3-*t*-17-dihydroxy χ tiocolenamides (IV), m.p. 294—296° (decomp.); this is transformed by Ac_2O in C_5H_5N at room temp. into the 3-*Ac* derivative, m.p. 269—270° (converted by $MgMeI$ in Et_2O into Δ^5 -17-methylandrosterone-3:17-diol), and hydrolysed ($NaOPr^a$ in boiling Pr^aOH) to Δ^5 -3-*t*-17-dihydroxy χ tiocolenic acid, new m.p. 267—268° (decomp.) [Me ester, m.p. 191—192° (acetate, m.p. 200—201°), Ac_2 derivative, m.p. 219—220° (Me ester, m.p. 144—145°)]. (III) and $EtOH \cdot CHCl_3 \cdot HCl$ at 60° give (IV) and 5-chloro-3:17-diacetoxy χ tiocolenamides (?), decomp. 200°.

H. W.

Tauroapochenodeoxycholic acid from the bile of hens. K. TAKAHASHI (Z. physiol. Chem., 1938, 255, 277—280; cf. Yonemura, A., 1928, 756).—Purified hen's bile with dil. HCl at 0° gives tauroapochenodeoxycholic acid, $C_{26}H_{43}O_5NS$, m.p. 210°, $[\alpha]_D^{20} +45.6^\circ$ in $EtOH$, which, with 10% aq. KOH at 130—140° for 6 hr. gives apochenodeoxycholic acid (I) (probably 3-hydroxy- $\Delta^{8:14}$ -cholenic acid), $C_{24}H_{38}O_3$, m.p. 160°, $[\alpha]_D^{20} +71.0^\circ$ in $EtOH$ (acetate, m.p. 152°), which is probably not a natural product but is produced during the hydrolysis as a result of loss of OH from C_{17} . (I) could not be reduced catalytically but it is oxidised ($CrO_3 \cdot AcOH$) to dehydroapochenodeoxycholic (3-ketocholenic) acid, $C_{24}H_{36}O_3$, m.p. 140°

(*oxime*, decomp. 188—190°). (I) heated at 250—360° in a high vac. yields *apochenodeoxycholadienic acid*, $C_{24}H_{36}O_2$, m.p. 133°, $[\alpha]_D^{20} +93.7^\circ$ in EtOH, reduced (H_2 , PtO₂, AcOH at 28°) to β -cholenic acid.

W. McC.

Chelate compounds. III. Inner-complex iron and manganese salts of the hydroxyaldimines. T. TSUMAKI (Bull. Chem. Soc. Japan, 1938, **13**, 579—582).—An account of work previously reviewed (A., 1937, II, 247).

F. J. G.

Chelate compounds. V. Spectrochemical studies on the inner-complex metallic salts of salicylaldehyde-ethylenedi-imine and related compounds. T. TSUMAKI (Bull. Chem. Soc. Japan, 1938, **13**, 583—591; cf. A., 1938, II, 191).—The extinction curves for a no. of inner-complex Cu, Ni, Mg, and Fe^{III} salts of salicylaldehyde-ethylenedi-imine and related imines have been determined and compared with those for the parent substances. It is concluded that they have an asymmetric configuration, the two O of the org. residue occupying *trans* co-ordination positions.

F. J. G.

Occurrence of more than two polymorphous, crystalline-liquid phases among azomethine compounds. C. WEYGAND and R. GABLER (J. pr. Chem., 1938, [ii], **151**, 215—220).—Among compounds $p\text{-OEt}\cdot C_6H_4\cdot N\text{:CH}\cdot C_6H_4\cdot OR\cdot p$ ($R = \text{Me}$ to hexadecyl), a single cryst.-liquid phase, apparently a Pl form, is observed in each case from the Me to the *n*-octyl derivative. In the cases of the *n*-nonyl derivative the m.p. (cryst. solid) is close to the temp. of clarification. The compound can be considerably undercooled and in this region two cryst.-liquid phase transitions (both probably Bz forms) can be observed. With falling temp. the three cryst.-liquid modifications can be observed under a cover glass or with unprotected specimens but only in the droplets when the temp. is rising. $p\text{-OH}\cdot C_6H_4\cdot \text{CHO}$ is transformed by nonyl iodide in boiling KOH-MeOH in to *p-n-nonoxybenzaldehyde*, b.p. 181°/4 mm., which with $p\text{-OEt}\cdot C_6H_4\cdot \text{NH}_2$ in EtOH gives *p-n-nonoxybenzylidenephenetidine*, m.p. 101—102°. H. W.

meso-Aldehydes of anthracene and 1:2-benzanthracene. L. F. FIESER and J. L. HARTWELL (J. Amer. Chem. Soc., 1938, **60**, 2555—2559).— $\text{NPhMe}\cdot\text{CHO}$, POCl₃, and anthracene (I) in $o\text{-C}_6\text{H}_4\text{Cl}_2$ at 100° give 92% of 9-anthraldehyde (II), m.p. 98.4—99.4° (lit. 104—105°) (cf. Vollmann *et al.*, A., 1937, II, 450). Under similar conditions 1:2-benzanthracene (best purified by adsorption on to Al₂O₃) gives 64% of 1:2-benzanthracene-10-aldehyde (III), m.p. 147.5—148°, but 1:2:5:6-dibenzanthracene does not react even at 155°, which confirms the hindrance at the *meso*-positions. The hydrazone of (II) is reduced (NaOEt-EtOH at 205°) to 9-methylantracene; the *oxime*, m.p. 165—165.5° (lit., 186—187°), with Ac₂O gives 9-cyanoanthracene, m.p. 177.5—179° (lit., 170—172°), but with AcCl yields the *oxime acetate*, m.p. 131.5—132°. With $\text{CH}_2(\text{CO}_2\text{H})_2$ and a little $\text{C}_2\text{H}_5\text{N}$ at 100° (II) gives 9-anthrylidene-maleonic acid, yellow, anhyd. and orange, hydrated forms, m.p. 240—246° (decomp.) (Me_2 ester, m.p. 134.5—135.5°), resistant to decarboxylation. With MgMeI (II) gives α -9-anthranylethyl alcohol, m.p. 125—126.5°,

converted by KHSO₄ into a tar containing (I), by the Tschugaev reaction into (I) and 9-ethylanthracene [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ additive compound, m.p. 125.3—125.6°], and by P₂O₅ in hot C_6H_6 into *di-(α -9-anthranylethyl) ether*, m.p. 247.5—248° after softening (with CrO₃ yields anthraquinone). The *hydrazone*, m.p. 187.5—188°, of (III) with NaOEt-EtOH gives a quant. yield of 10-methyl-1:2-benzanthracene; the *oxime*, double m.p. 203.5—204.5° and 231—232.5° (decomp.), gives 10-cyano-1:2-benzanthracene, m.p. 188.5—189.5°. With MgMeI (III) gives α -1:2-benz-10-anthranylethyl alcohol, m.p. 148—150°. M.p. are corr. R. S. C.

Synthetic analeptics resembling lobeline. K. WARNAT (Festschr. E. C. Barell, Basel, 1936, 255—265; Chem. Zentr., 1936, ii, 3911).—Compounds structurally related to, but simpler than, lobeline [2- β -hydroxy- β -phenylethyl-6-phenacyl-1-methylpiperidine] are synthesised from, e.g., $\text{OH}\cdot\text{CHPh}\cdot\text{CHR}\cdot\text{NHMe}$ ($R = \text{H, Me}$) and $\text{COPh}\cdot\text{CHAlkBr}$. *l*-Ephedrine (I) (in $\text{C}_6\text{H}_6 + \text{H}_2\text{O}$) heated with $\text{COPh}\cdot\text{CHMeBr}$ and conc. KOH gives 1- α -benzylethyl-(β -hydroxy- β -phenylisopropyl)methylamine (II), m.p. 126° (hydrochloride, m.p. 193°); crude (II) when heated affords the *dl*-compound, m.p. 93° (prep. from *dl*-ephedrine). An *isomeride*, m.p. 156° (hydrochloride, m.p. 206°), of (II) is similarly obtained using *d- ψ* -ephedrine; it is dehydrated by boiling conc. HCl to an unstable base, $\text{C}_{19}\text{H}_{21}\text{ON}$. $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Cl}$ with (I) (in PhMe at 100°) and deoxy-ephedrine (at 160°) gives respectively β -phenylethyl-(β -hydroxy- β -phenylisopropyl)- and -(β -phenylisopropyl)-methylamine (hydrochlorides, m.p. 173—174° and 171°, respectively). α -Benzylethyl-(β -methoxy- β -phenylisopropyl)methylamine (hydrochloride, m.p. 130°) (from $\text{OMe}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NHMe}$ and $\text{COPh}\cdot\text{CHMeBr}$) and 1- α -anisylethyl-(β -hydroxy- β -phenylisopropyl)methylamine, m.p. 133—134° (hydrochloride, m.p. 163°) [from (I) and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHMeBr}$], are prepared as (II). Paraformaldehyde, COPhMe , and $\text{NH}_2\text{Me}\cdot\text{HCl}$ in EtOH give *di- β -benzylethylmethylamine*, m.p. 141° (hydrochloride, m.p. 169°) (could not be reduced to the CO-alcohol), together with 4-hydroxy-3-benzoyl-4-phenyl-1-methylpiperidine, m.p. 142° [hydrochloride, m.p. 191°; methiodide, m.p. 183°; Bz derivative (hydrochloride, m.p. 237—240°; methiodide, m.p. 226°)]. Of all the compounds tested pharmacologically, (II) is the most useful. H. B.

Chalkones. Condensation of aromatic aldehydes with resacetophenone. I. Z. SAYAD, D. R. NADKARNI, and T. S. WHEELER (J.C.S., 1937, 1737—1739).—Contrary to various statements (lit.), resacetophenone with PhCHO and protocatechualdehyde in EtOH-KOH gives respectively 2:4-dihydroxyphenyl styryl ketone, m.p. 150°, and butein. These chalkones may be converted into the hydroxy-flavanones by the use of dil. alkali (cf. A., 1938, II, 452).

F. R. S.

Ethylenic stereoisomerism. II. Formation of β -methoxy- and β -ethoxy-chalkone from α -bromochalkone and from dibenzoylmethane. C. WEYGAND and W. LANZENDORF (J. pr. Chem., 1938, [ii], **151**, 227—230).—Cryst. α -bromochalkone, m.p. 42°, when treated according to Weygand *et al.* (A., 1929, 564), gives β -methoxychalkone, m.p. 65°, with

considerable amounts of $\text{COPh}\cdot\text{CH}_2\cdot\text{CPh}(\text{OMe})_2$. β -Methoxychalkone, m.p. 81° , is formed exclusively from CH_2Bz_2 and CH_2N_2 in Et_2O . With CHMeN_2 the metastable polymorphic modification, m.p. 63.5° , of β -ethoxychalkone is now obtained from CH_2Bz_2 in place of the modification, m.p. 78° , obtained previously (*loc. cit.*). Etherification by N_2 -compounds is regarded as configuration-sp. H. W.

Phenanthrene series. XVIII. Synthesis of acyl compounds derived from 1- and 4-phenanthrol. H. M. DUVAL and E. MOSETTIG (J. Amer. Chem. Soc., 1938, 60, 2409—2413).—2-Acetyl- (I), m.p. 154 — 155° , and 2-propionyl-1-phenanthrol (II), m.p. 149 — 150° , are obtained in 60 and 72% yield, respectively, from 2-acetoxy-, m.p. 131 — 134° , and 2-propionoxy-phenanthrene, respectively, by AlCl_3 in PhNO_2 , but in only 30 and 26% yield, respectively, by the Friedel-Crafts reaction in PhNO_2 . However, γ -acetyl-4-phenanthrol, m.p. 112 — 113° , is obtained in only 30% yield with a little (?) diacetyl-4-phenanthrol (III), m.p. 193° [dioxime, m.p. 228 — 229° (decomp.)], by Fries rearrangement of 4-acetoxyphenanthrene, m.p. 58 — 60° , and the Friedel-Crafts reaction gives 60—70% yields of (III) and dipropionyl-4-phenanthrol, m.p. 165 — 165.5° , as sole product. 4-Methoxyphenanthrene gives (Friedel-Crafts) 70% of α -acetyl- (IV), m.p. 122.5 — 123.5° , and α -propionyl-4-methoxyphenanthrene (V), m.p. 116° , but 1-methoxyphenanthrene gives only tars. The *Me* ether (VI), m.p. 81 — 81.5° , of (I) or (m.p. 74 — 76°) of (II) with NaOCl gives 1-methoxyphenanthrene-2-carboxylic acid, m.p. 224 — 225° (decomp.) (*Me* ester, m.p. 109 — 110°). The oxime, m.p. 166 — 167° (decomp.), of (VI) and HCl - AcOH - Ac_2O at room temp. give 2-acetamido-1-methoxyphenanthrene, m.p. 222 — 223° (decomp.), hydrolysed by 6N - HCl to 2-amino-1-methoxyphenanthrene, m.p. 139.5 — 141° , diazotisation of which gives 10% of 1-phenanthrol as sole product. The oxime, m.p. 224 — 225° (decomp.), of (I) is converted by PCl_5 into 2-acetamido-1-hydroxyphenanthrene, which by hydrolysis, oxidation, reduction, and methylation affords 1:2-dimethoxyphenanthrene. With NaOCl (IV) or (V) gives 4-methoxyphenanthrene- α -carboxylic acid, m.p. 238 — 239° (*Me* ester, m.p. 93 — 94°). The oxime, m.p. 190 — 191° (decomp.), of (IV) with HCl - AcOH - Ac_2O gives α -acetamido-4-methoxyphenanthrene, m.p. 201° . R. S. C.

Addition reactions of unsaturated α -keto-acids. V. (MISSES) M. REIMER and E. CHASE (J. Amer. Chem. Soc., 1938, 60, 2469—2471; cf. A., 1935, 490).—*p*-Me affects the additive reactions of $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ less than, but similarly to, *p*-OMe. *p*-Tolylidenepyruvic acid (I) (prepared from ACCO_2H and $\text{C}_6\text{H}_4\text{MeCHO}$ in 25% KOH - MeOH at 10°), m.p. (anhyd.) 127° and (+ xH_2O) ~ 100 — 110° (softens at $\sim 80^\circ$), unstable (*Me*, m.p. 81° , and *Et* ester, m.p. 44 — 46°), gives the dibromide, m.p. 145 — 147° (*Me* ester, m.p. 86 — 87°), which in hot H_2O rapidly gives β -bromo-*p*-tolylidenepyruvic acid (II), m.p. 182° (*Me* ester, m.p. 77° , prepared by CH_2N_2), oxidised by alkaline H_2O_2 to α -bromo-*p*-methylcinnamic acid, m.p. 192° (*Me* ester, m.p. 36 — 37°) (cf. Gattermann, A., 1906, i, 589). H_2O_2 oxidises (I) to *p*-methylcinnamic acid [dibromide, m.p. 192° (*Me* ester, m.p. 101°), and

an isomeride (not obtained pure)]. With H_2SO_4 rather weak colours are given by (I), the Br-acids, and their esters. *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ and Br-MeOH give the β -Br-derivative and OMe- $\text{C}_6\text{H}_3\text{Br}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{Me}$; with (I) no ring-bromination occurs, the main product being (II).

R. S. C.

Friedel-Crafts condensation with arylalkylene ether chlorides. H. A. BRUSON and J. W. EASTES (J. Amer. Chem. Soc., 1938, 60, 2502—2505).—The Cl in $\text{OR}\cdot[\text{CH}_2]_2\text{Cl}$ is unreactive in the Friedel-Crafts reaction, which may be carried out normally with other reactants if R is or contains an aromatic group. Thus, $\text{OPh}\cdot[\text{CH}_2]_2\text{O}\cdot[\text{CH}_2]_2\text{Cl}$ (I), $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$, and AlCl_3 in CS_2 give *o*-(β - β' -chloroethoxyethoxybenzoyl)-benzoic acid, m.p. 124° . *o*- β -Chloroethoxybenzoyl-, m.p. 145° , *o*-(3-chloro-4- β - β' -chloroethoxyethoxybenzoyl)-, m.p. 85° , *o*-(4- β - β' -chloroethoxyethoxy-3-methylbenzoyl)-, m.p. 87 — 88.5° , *o*-(4- β - β' -chloroethoxyethoxy-*m*-anisoyl)-, m.p. 188 — 190° , and *o*-(2- β - β' -chloroethoxyethoxy-1-naphthoyl)-benzoic acid, m.p. 125° , are similarly obtained. An attempt to prepare $\text{o-Cl}\cdot[\text{CH}_2]_2\text{O}\cdot[\text{CH}_2]_2\text{O}\cdot[\text{CH}_2]_2\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ gave a syrup. With $(\text{CH}_2\text{CO})_2\text{O}$, $(\text{CH}\cdot\text{CO})_2\text{O}$, AcCl or Ac_2O , and Bu^+Cl (I) gives β - β' -(β - β' -chloroethoxyethoxybenzoyl)-propionic, m.p. 97 — 98° , and -acrylic acid, m.p. 100° , *p*-(β - β' -chloroethoxyethoxy)-acetophenone, b.p. 210 — $222^\circ/10$ mm., and *n*-butylbenzene, b.p. 170 — $185^\circ/9$ mm., respectively. With diisobutene and conc. H_2SO_4 (I) gives β - β' -(β - β' -chloroethoxyethoxy- α - γ -tetramethyl-*n*-butylbenzene, b.p. 157 — $161^\circ/1$ mm., also obtained from $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{O}$ and *p*- $\text{CH}_2\text{Bu}^+\text{CMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$. With β -octanol and a surface-active clay at 180° (I) gives α -methyl-*n*-heptyl-phenyl β - β' -(β - β' -chloroethoxyethoxyethyl ether, b.p. 175 — $185^\circ/3$ mm., and $\text{OPh}\cdot[\text{CH}_2]_2\text{Cl}$ and $\text{C}_{12}\text{H}_{25}\text{OH}$ give similarly β -*n*-dodecylphenoxyethyl chloride, b.p. 185 — $195^\circ/1$ mm. R. S. C.

Photolysis of cyclic ketones in the gas phase.—See A., 1938, I, 632.

Reactions catalysed by aluminium chloride. XVII. Mechanism of the condensation of carbon monoxide with cyclohexane. C. D. NENITZESCU and D. V. CURCANEANU (Ber., 1938 71, [B], 2063—2065; cf. A., 1936, 1485).—1-Acetyl-1-methylcyclopentane is oxidised (KMnO_4 and NaOH at room temp.) to 1-methylcyclopentyl-1-glyoxylic acid, b.p. 113 — $114^\circ/10$ mm. [semicarbazone, m.p. 167 — 168° (decomp.); NH_2Ph salt, m.p. 135.5°], converted by distillation with NH_2Ph and subsequent hydrolysis into 1-methylcyclopentane-1-aldehyde (I), b.p. 142 — 143° (semicarbazone, m.p. 160 — 161°). The conversion of this by AlCl_3 in cyclohexane (II) into 2-methylcyclohexanone (III) shows that the action of CO on cyclohexane follows the course: (II) \longleftrightarrow methylcyclopentane \rightarrow 1-methyl- Δ^1 -cyclopentene \rightarrow 2-chloro-1-methylcyclopentane-1-aldehyde \rightarrow (I) \rightarrow (III).

H. W.

Heteropolarity. XXXIV. Dinitrophenylhydrazones of dark-coloured ketones with five-membered rings. W. JOSTEN (Ber., 1938, 71, [B], 2230—2231).—Tetracyclone and 2:4-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ in boiling dioxan-conc. H_2SO_4 and N_2 give the corresponding 2:4-dinitrophenyl-

hydrazone, m.p. 271°. The 2:4-dinitrophenylhydrazones of phencyclone and acecyclohexane have m.p. 318° (decomp.) and 335—337°, respectively. H. W.

Ethylenic stereoisomerism. I. Stereoisomeric homologous dibenzoylethylenes and the corresponding dibenzoylethanes. C. WEYGAND and W. LANZENDORF (J. pr. Chem., 1938, [ii], 151, 204—214).—*pp'*-Dialkyldibenzoylethylenes are obtained by the gradual addition of fumaryl chloride and the requisite PhAlk to AlCl_3 in CS_2 at room temp. The corresponding unilaterally substituted compounds cannot be obtained from BzCHO or $\text{CHBz}(\text{OH})_2$ and *p*- $\text{C}_6\text{H}_4\text{Alk-COMe}$ in Ac_2O and are prepared in AcOH containing a little conc. H_2SO_4 . The yellow modifications (I) are thus obtained; they pass into the colourless forms (II) when irradiated and are re-formed by the action of HCl on the latter. A close relationship in m.p. appears to exist between (I) and the corresponding dibenzoylethanes, conforming thus to Bruni's rule according to which *trans* forms are more closely related morphologically than *cis* forms to their H_2 -derivatives. The higher (I) appear incapable of forming diphenylpyridazines, thus indicating their *trans* structure. The following *-dibenzoylethylenes* are described [the m.p. of the (I) precede those of (II)]: *pp'*-dimethyl-, m.p. 148.5°, 125°; *pp'*-diethyl-, m.p. 114.5°, 109°; *pp'*-di-*n*-propyl-, m.p. 109.5°, 56°; *pp'*-di-*n*-butyl-, m.p. 98°, 51°; *pp'*-di-*n*-amyl-, m.p. 98.5°, 52°; *pp'*-di-*n*-hexyl-, m.p. 99.5°, 46° [all these compounds give *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ when oxidised]; *p*-methyl-, m.p. 86.5°, 109°; *p*-ethyl-, m.p. 76.5°, 86.5°; *p*-*n*-propyl-, m.p. 68.5°, 71.5°; *p*-*n*-butyl-, m.p. 57°, 57.5°; *p*-*n*-amyl-, m.p. 53.5°, 54°. Catalytic reduction of (I) does not proceed satisfactorily but they are converted by $\text{Na}_2\text{S}_2\text{O}_4$ in EtOH into the following *-dibenzoylethanes*: *pp'*-diethyl-, m.p. 126°; *pp'*-dipropyl-, m.p. 117°; *pp'*-dibutyl-, m.p. 115°; *pp'*-diamyl-, m.p. 114°; *p*-methyl-, m.p. 121°; *p*-ethyl-, m.p. 91.5°; *p*-propyl-, m.p. 86.5°; *p*-butyl-, m.p. 85°; *p*-amyl-, m.p. 83.5°. BzCHO and COPhMe in boiling Ac_2O afford α -acetoxy- $\alpha\beta$ -dibenzoylethane (III), m.p. 112°, which at 200° gives AcOH and yellow dibenzoylethylene. Gradual addition of BzCHO in AcOH to a boiling solution of COPhMe in AcOH gives $\alpha\beta$ -dibenzoylethanol, m.p. 93.5°, transformed by warm Ac_2O into (III). H. W.

Ethylenic stereoisomerism. III. Rates of hydrogenation of *cis*- and *trans*-isomerides. C. WEYGAND, A. WERNER, and W. LANZENDORF (J. pr. Chem., 1938, [ii], 151, 231—232).—The yellow, stable, presumably *trans*-(CHBz)₂ is more slowly hydrogenated (PtO_2 in AcOH) than the colourless, presumably *cis*-isomeride; the same relationship is observed with the *pp'*- Me_2 and *pp'*- Bu_2 derivatives. When substitution is one-sided the relationship is reversed, the yellow *p*-methyl- and *p*-*n*-butyl-dibenzoylethylene absorbing H_2 more rapidly than the colourless isomerides. Since there is no doubt that the yellow forms in each series correspond sterically, the differing rates of hydrogenation of ethylenic stereoisomerides must be influenced by constitutive (particularly as regards symmetry) as well as by configurative factors. A general rule for

the elucidation of the configuration of ethylenic stereoisomerides cannot therefore be based on the rate of hydrogenation. H. W.

Action of aluminium chloride on diphenyl isophthalate, terephthalate, and naphthalate. F. F. BLICKE and R. A. PATELSKI (J. Amer. Chem. Soc., 1938, 60, 2283—2285).—*m*- $\text{C}_6\text{H}_4(\text{CO}_2\text{Ph})_2$, m.p. 137—138° (lit., 120°), and AlCl_3 in hot CS_2 give 1:3-di-*p*-hydroxybenzoylbenzene, m.p. 207—209° (lit., 215°) [purified by way of the Ac_2 derivative, m.p. 189—190°; (*m*- $\text{C}_6\text{H}_4\text{Br-CO}$)₂ derivative, m.p. 234—235°], also obtained as sole product (cf. Weiss *et al.*, A., 1935, 753) from *m*- $\text{C}_6\text{H}_4(\text{COCl})_2$, PhOMe , and AlCl_3 in CS_2 . *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{Ph})_2$ and AlCl_3 give similarly 1:4-di-*p*-hydroxybenzoylbenzene, m.p. 297—299° [Ac_2 , m.p. 249—250°, and (*m*- $\text{C}_6\text{H}_4\text{Br-CO}$)₂ derivative, m.p. 289—291°; dioxime, m.p. 261—263°; Me_2 ether, m.p. 225—227° (lit. 236—239°)], also obtained from *p*- $\text{C}_6\text{H}_4(\text{COCl})_2$, PhOMe , and AlCl_3 . However, Ph_2 naphthalate (prep. from the anhydride, POCl_3 , PCl_5 , and, later, PhOH), m.p. 150—151°, behaves like *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{Ph})_2$ (Blicke *et al.*, A., 1932, 273), giving with AlCl_3 phenolnaphthalen, m.p. 265—266° (decomp.), obtained also from 8-*p*-hydroxybenzoyl-1-naphthoic acid, m.p. 219—220°, by AlCl_3 and PhOH at 150—160° or (with this acid) from 1:8- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{O})_2$, PhOH , and AlCl_3 at 100°.

R. S. C.

Interaction of diphenic anhydride with phenols and hydrocarbons. F. BELL and F. BRIGGS (J.C.S., 1938, 1561—1568).—Diphenic anhydride (I) reacts with phenols, phenol ethers, and some aromatic hydrocarbons to give 2:2'-diaroyldiphenyls and 2-aroyldiphenyl-2'-carboxylic acids (cf. Dutt, J.C.S., 1923, 123, 225; Underwood *et al.*, A., 1924, i, 176, 1197; 1929, 444; 1936, 723). Colour reactions and absorption spectra of the "diphenesins" (cf. Underwood, *loc. cit.*) are different from those of the phthal-*ins* and there is no evidence for the presence of the lactone ring. Unless stated otherwise, (I), the phenol, and SnCl_4 are heated at 120° for 5—6 hr. PhOH affords 2:2'-di-*p*-hydroxybenzoyldiphenyl (II), m.p. 245°, and a little 2-*p*-hydroxybenzoyldiphenyl-2'-carboxylic acid (III), m.p. 223°, which gives (II) with PhOH-SnCl_4 at 120° for 5 hr. (II) and Me_2SO_4 -aq. NaOH give 2:2'-dianisoyldiphenyl (does not react with NHPh-NH_2 etc.), also obtained from PhOMe and ($\text{C}_6\text{H}_4\text{-COCl}$)₂. (I) and PhOH alone at 125° for 5 hr., or (I) and $\text{PhOH-AlCl}_3\text{-C}_6\text{H}_6$ at room temp., afford *Ph H diphenate*, m.p. 139°, which with AlCl_3 in $\text{C}_2\text{H}_5\text{Cl}_4$ at 120°/1 hr., or in H_2SO_4 at 100°/¼ hr., gives fluoronone-4-carboxylic acid (IV) (+ diphenic acid in former case), also obtained from (III) and H_2SO_4 at 150° for ¼ hr. (I) and $\text{PhOH-H}_2\text{SO}_4$ at 115° for 5 hr. give (III).

(I) and *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ yield (cf. Bischoff and Adkins, A., 1923, i, 578) 2:2'-bis-2'':4''-dihydroxybenzoyldiphenyl (+ EtOH), m.p. 180° (decomp.), m.p. ("anhyd.") 256° (cf. "resorcinoldiphenicins," m.p. 180°; Underwood, *loc. cit.*), methylated (Me_2SO_4 - NaOH) to the bis-2'':4''-(OMe)₂-compound, m.p. 140—142°, also obtained from ($\text{C}_6\text{H}_4\text{-COCl}$)₂, *m*- $\text{C}_6\text{H}_4(\text{OMe})_2$, and AlCl_3 . *o*-, *m*-, and *p*-Cresol yield respectively 2:2'-bis-6''-hydroxy-*m*-toluoyldiphenyl

and 2-6''-hydroxy-m-toluyldiphenyl-2'-carboxylic acid, m.p. 207° [gives (IV) with H_2SO_4 at 120° for $\frac{1}{4}$ hr.] (cf. Underwood, 1936); 2:2'-bis-5''-hydroxy-o-toluyldiphenyl, m.p. 147°, and an isomeride (+ EtOH), decomp. 123—125°; and 2:2'-bis-4''-hydroxy-m-toluyldiphenyl, m.p. 205°, and 2-4''-hydroxy-m-toluyldiphenyl-2'-carboxylic acid, m.p. 190—194°. o-4-, m-4-, and p-Xylenols yield 2:2'-bis-2''-hydroxy-4'' : 5''-dimethylbenzoyldiphenyl, m.p. 163°, and 2-2''-hydroxy-4'' : 5''-dimethylbenzoyldiphenyl-2'-carboxylic acid, m.p. 177°; 2:2'-bis-2''-hydroxy-3'' : 5''-dimethylbenzoyldiphenyl, m.p. 168°; and 2:2'-bis-4''-hydroxy-2'' : 5''-dimethylbenzoyldiphenyl, m.p. 252°, and 2-4''-hydroxy-2'' : 5''-dimethylbenzoyldiphenyl-2'-carboxylic acid, m.p. 245°. Thymol affords 2:2'-bis-4''-hydroxy-2''-methyl-5''-isopropylbenzoyldiphenyl, m.p. 258°, and 2-4''-hydroxy-2''-methyl-5''-isopropylbenzoyldiphenyl-2'-carboxylic acid, m.p. 245°. Quinol, 1:2:3- or 1:3:5- $\text{C}_6\text{H}_3(\text{OH})_3$ afford no pure product. p- $\text{C}_6\text{H}_4\text{Hal}\cdot\text{OH}$ behave differently and afford p-chlorophenyl, m.p. 89°, and p-bromophenyl, m.p. 100°, diphenate. PhOMe and PhOEt with (I) and AlCl_3 yield respectively 2-anisoyl-, m.p. 155° (+ some 2:2'-dianisoyldiphenyl), and 2-p-ethoxybenzoyl-, m.p. 178—180°, -diphenyl-2'-carboxylic acid, converted by H_2SO_4 at 120° for $\frac{1}{4}$ hr. into (IV), and also 4-anisoylfluorenone, m.p. 115°, and (III), respectively.

(I), C_{10}H_8 (in C_6H_6), and AlCl_3 for 12 hr. give 2-naphthoyldiphenyl-2'-carboxylic acid, m.p. 180°; o-, m-, and p-xylene similarly (4 hr.) afford 2-3'' : 4''-, m.p. 114—117° (aq. EtOH), 93—95° (AcOH), 2-2'' : 4''-, m.p. 194°, and 2-2'' : 5''-, m.p. 163—165°, -dimethylbenzoyldiphenyl-2'-carboxylic acids, respectively, in the last case with some 2:2'-bis-2'' : 5''-dimethylbenzoyldiphenyl, m.p. 148°, also obtained from $(\text{C}_6\text{H}_5\cdot\text{COCl})_2$, AlCl_3 , and p-xylene. The last three carboxylic acids and H_2SO_4 at 120°, 150°, and 120°, respectively, for $\frac{1}{4}$ hr. afford 4-3' : 4'-dimethylbenzoylfluorenone, m.p. 144° [also from the chloride of (IV), o-xylene and AlCl_3], (IV), and 4-2' : 5'-dimethylbenzoylfluorenone, m.p. 143°, respectively. s- $\text{C}_6\text{H}_3\text{Me}_3$, (I), and AlCl_3 (4 hr.) give 2-2'' : 4'' : 6''-trimethylbenzoyldiphenyl-2'-carboxylic acid, m.p. 213°, converted by H_2SO_4 at 100° into (IV). C_6H_6 , PhMe, and PhEt do not condense with (I); Ph₂ gives non-cryst. material. (IV) and KOH at 200—220° give diphenyl-2:6-dicarboxylic acid, m.p. 282°, and (IV) and PhOH- H_2SO_4 at 115° for 8 hr. give 9:9-di-p-hydroxyphenylfluorene-4-carboxylic acid, m.p. 276—279° (decomp.) (cf. Underwood, 1924).

A. T. P.

Derivatives of decahydronaphthalene. I. K. GANAPATI (J. Indian Chem. Soc., 1938, 15, 407—415; cf. Rao and Kuppuswamy, A., 1938, II, 15).—Partly a more detailed account of work previously reviewed (A., 1938, II, 286). The following appears new. *trans*-2:3-Diketodecahydronaphthalene (I), m.p. 100—101° (enol benzoate, m.p. 133°), with 4:5-diamino-uracil and -thiouracil gives the corresponding quinoxalines, m.p. ~315° and 295°, respectively. (I) and Na-Hg in aq. MeOH for 2—3 hr. afford 2:3-dihydroxy- (II), m.p. 141°, and 3-hydroxy-2-keto- (III), m.p. 134°, -*trans*-decahydronaphthalene, whilst Al-Hg gives an isomeride, m.p. 126°, of (II).

The stereochemistry of the $(\text{OH})_2$ -compounds is discussed; the OH are probably in *trans*-positions. 3-Bromo-2-keto-*trans*-decahydronaphthalene (IV), m.p. 150°, is stable to alkaline hydrolysis; a trace of (III) may be formed. AcOH-KOAc at 170—180° for 5 hr. afford a compound, m.p. 122°, reconverted into (IV) by boiling alkali. (?) 3:3-Dibromo-2-keto-*trans*-decahydronaphthalene is slowly converted by boiling 20% aq. KOH into *trans*-2-hydroxyhexahydroindene-2-carboxylic acid. A. T. P.

Isomerisation and dismutation of hydroxy-keto-compounds having a cyclopentanopolycyclophenanthrene skeleton.—See B., 1938, 1365.

Experiments on the synthesis of substances related to the sterols. XXI. New synthesis of derivatives of ketocyclopentenophenanthrene. R. ROBINSON (J.C.S., 1938, 1390—1397).—Furfuraldehyde (I), acetoveratrone, and aq. EtOH-NaOH afford furfurylideneacetoveratrone, m.p. 81°, hydrolysed by aq. HCl-EtOH to γ -diketo- ζ -3:4-dimethoxyphenylheptonic acid, m.p. 126°. Hydrolysis of furfurylideneacetophenone, m.p. 47° (cf. lit.), gives γ -diketo- ζ -phenylheptonic acid (Kehrer *et al.*, A., 1899, i, 568), which when boiled with aq. KOH affords 3-phenyl- Δ^2 -cyclopenten-1-one-2-acetic acid (II), m.p. 141° [2:4-dinitrophenylhydrazones, m.p. 273° (decomp.)]. This with Na-EtOH gives the lactone, b.p. 153°/0.15 mm., of 3-phenylcyclopentan-1-ol-2-acetic acid and some oily OH-acids. With conc. and then dil. H_2SO_4 at 100°, (II) is converted into 4-hydroxy-3'-keto-1:2-cyclopentenonaphthalene, m.p. 290—295° (decomp.) [2:4-dinitrophenylhydrazones, darkens at >200° and decomp. at 305° to a black tar; p-nitrobenzeneazoderivative, m.p. 245° (decomp.)], but with H_2SO_4 at 140° a different substance, m.p. 290°, is obtained. By similar methods 2- $\text{C}_{10}\text{H}_7\text{Ac}$ and (I) give furfurylidene-2-acetylnaphthalene, m.p. 91°, hydrolysed to γ -diketo- ζ - β -naphthylheptonic acid, m.p. 167—169° [bis-2:4-dinitrophenylhydrazones, m.p. 250° (decomp.)]; disemicarbazone, m.p. 183—184° (decomp.)], converted by aq. KOH into 3- β -naphthyl- Δ^2 -cyclopenten-1-one-2-acetic acid, m.p. 168—169°, oxidised by alkaline KMnO_4 to β - $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$, and converted by boiling Ac_2O into 4-acetoxy-3'-keto-1:2-cyclopentenophenanthrene (III), m.p. 207°. This is hydrolysed to the corresponding 4-hydroxy-ketone, m.p. 310—315° (previous darkening and softening) [oxime, m.p. 271° (decomp.)]; anisylidene derivative, decomp. 305—310°], the Me ether, m.p. 179°, of which with o-vanillin and HCl in EtOAc followed by FeCl_3 gives 8:4'-dimethoxyphenanthracyclopentadienochromylum ferrichloride, shrinks at 245—248°. Reduction (Clemmensen) of (III) gives a phenol which when distilled with Zn dust in H_2 gives a mixture of hydrocarbons, m.p. ~160°. With CrO_3 -AcOH (III) gives a substance, m.p. >350°, probably impure 2-carboxy-4-hydroxyphenanthraquinone-1-acetic acid, and other phenanthraquinone derivatives. 2:6- $\text{C}_{10}\text{H}_6\text{Ac}\cdot\text{OMe}$, m.p. 107° (lit. 105°), with (I) and NaOMe-MeOH gives furfurylidene-6-methoxy-2-acetylnaphthalene, m.p. 113°, hydrolysed by HCl-EtOH to γ -diketo- ζ -(β -6'-methoxynaphthyl)heptonic acid, m.p. 142—143°, from which 3-(6'-methoxy- β -naphthyl)- Δ^2 -cyclopenten-1-one-2-acetic acid, m.p. 204—205°, 3'-keto-4-acetoxy-7-

methoxy-1:2-cyclopentenophenanthrene, m.p. 254° after shrinking at 250°, and the corresponding 4-*hydroxy-ketone*, m.p. 293—299° (previous darkening and softening) [*Me ether*, m.p. 200—201° (softens at 195°)], were successively obtained. H. G. M.

Sterol group. XXXVIII. Bromination of 6-keto-3-acetoxy- Δ^4 -cholestene. H. JACKSON and E. R. H. JONES (J.C.S., 1938, 1406—1408).—6-Keto-3-acetoxy- Δ^4 -cholestene (I) with Br (2 mols.) in AcOH gives 4:5-dibromo-6-ketocholestanyl acetate (II), m.p. 81—82° (decomp.), reconverted into (I) by boiling KI-COMe₂ or C₅H₅N. (I) in Et₂O with Br (1 mol.) in AcOH gives 4-bromo-6-keto-3-acetoxy- Δ^4 -cholestene (III), m.p. 115—116°, stable to KOAc—AcOH (100°; 1 hr.), KOAc—EtOH (b.p.; 12 hr.), and to AgNO₃ in C₅H₅N at 20° (48 hr.). When refluxed with AcOH—KOAc or dry Et₂O (II) is converted into (III). When refluxed (7 hr.) with anhyd. C₅H₅N, (III) yields 6-keto-3-acetoxy- $\Delta^{2:4}$ -cholestadiene. With NaOMe—MeOH at 20° (18 hr.), (II) and (III) give 3-hydroxy-6-keto-4:5-dimethoxycholestane, m.p. 149—150° (*monobenzoate*, m.p. 129—130°, softening at 126°). When heated with Zn dust in AcOH or EtOH, (III) gives 3:3'-bis-(6-keto- Δ^4 -cholesteryl), m.p. 257—258°, also obtained from (I) by similar means. Reduction (H₂, Pd-black, Et₂O) of (I) gives 6-ketocholestane (A., 1920, i, 434). H. G. M.

Sterols. XLIV. Pregnan-3-one and related compounds. R. E. MARKER and E. J. LAWSON (J. Amer. Chem. Soc., 1938, 60, 2438—2440; cf. A., 1938, II, 407).—Pregnan-3(α)-ol-2-one, dimorphous, m.p. 134° and 148° (2:4-dinitrophenylhydrazone, m.p. 229°), with Zn—Hg in hot HCl—AcOH gives a little pregnan-3(α)-ol (I), m.p. 148°, and much of its acetate, m.p. 106°. Clemmensen treatment of β -cholestanol gives mainly β -cholestyl acetate, but epicholestanol is unchanged. Hydrolysis should thus generally follow Clemmensen reduction of OH-ketones. With CrO₃ (I) gives mainly pregnan-3-one (II), m.p. 115° (*semicarbazone*, m.p. 133°; 2:4-dinitrophenylhydrazone, m.p. 163°), and some 3||4-pregnane-3:4-diacid (III), m.p. 297° (*Me₂ ester*, m.p. 147°). With H₂—PtO₂ and a little HBr in AcOH at 2.3 atm. (II) gives pregnan-3(β)-ol, m.p. 144° (*acetate*, m.p. 87°). 20-Keto-3||4-pregnane-3:4-diacid, m.p. 270° (2:4-dinitrophenylhydrazone, m.p. 210°) (Butenandt, A., 1932, 54), and Zn—Hg in HCl—AcOH give (III). R. S. C.

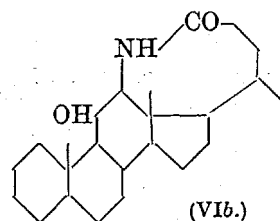
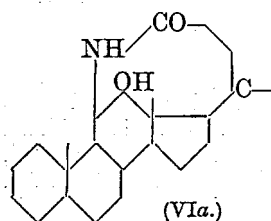
Isolation of progesterone and 3:20-allopregnanolone from ox adrenals. D. BEALL (Biochem. J., 1938, 32, 1957—1960).—The pentane-sol. material from the concentrate of ox adrenals (Reichstein, A., 1936, 1382) is saponified with MeOH—NaOMe in Et₂O at room temp., and the alkali-insol. material is separated into ketonic and non-ketonic fractions with "Girard reagent T." The ketonic fraction, separated by partitioning between light petroleum—70% EtOH and 70% EtOH—C₆H₆, yields 3:20-allopregnanolone (I) and a complex, m.p. 164—165°, of (I) with progesterone (II). (I) is separated from the complex by acetylation and saponification, whilst (II) is isolable from the filtrate after treatment with digitonin in 90% EtOH. J. D. R.

3-Keto-17-androstenyl carbonates.—See B., 1938, 1364.

R (A., II.)

Testosterone esters.—See B., 1938, 1365.

Cholanic acid derivatives with substituents in the 11- and 12-position. J. BARNETT and T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 926—939).—Technical deoxycholic acid is converted by the successive action of CH₂N₂ and *p*-C₆H₄Me·SO₂Cl—C₅H₅N into *Me* 3-*p*-toluenesulphonyldeoxycholate (I), m.p. 148° (corr.); *Me* 3-*p*-toluenesulphonylcholate, m.p. 131—133°, is obtained similarly. C₅H₅N and (I) at 140—150° (bath)/3 hr. give *Me* 12-hydroxy- Δ^3 -cholenate, m.p. 110—111° (corr.); protracted treatment with C₅H₅N or use of NPhMe₂ or quinoline gives poorer yields. This is hydrogenated (PtO₂ in MeOH—AcOH) to *Me* 12-hydroxycholenate, m.p. 120—121° (corr.), also obtained mixed with a stereoisomeride by reduction (Raney Ni) of *Me* 12-ketocholelate. It could not be esterified by *p*-C₆H₄Me·SO₂Cl in C₅H₅N. Bromination of 12-ketocholelate (cf. Wieland, *et al.*, A., 1931, 841) appears to give a mixture (II) of 11-bromo-12-ketocholelate acids, transformed by NaOAc in anhyd. AcOH at 190° into 12-keto- $\Delta^{9:11}$ -cholenic acid, m.p. 164—166° [*Me ester*, m.p. 92—93° (corr.), $[\alpha]_D^{25} + 86.9^\circ \pm 1.5^\circ$ in MeOH]. With KOH—MeOH (II) gives a mixture of 11-hydroxy-12-ketocholelate acids, α -form, m.p. 175—176° (corr.) [*Me ester* (III), m.p. 72—74°, $[\alpha]_D^{25} + 54.6^\circ \pm 1^\circ$ in MeOH], β -variety, m.p. 145—146° (corr.) [*Me ester* (IV), m.p. 106—107° (corr.), $[\alpha]_D^{25} + 58.5^\circ \pm 1^\circ$ in MeOH], best separated through the *Me esters*. CrO₃ in AcOH at room temp. oxidises (III) and (IV) to *Me* 11:12-diketocholelate (V), m.p. 102—103° (corr.), which is reduced (Zn dust, MeOH—AcOH) to (III) and (IV). Oximation of (V) gives a non-cryst. oxime-

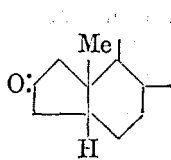


ester, hydrogenated (Raney Ni in MeOH at 100°/80 atm.) to the *OH-lactam* (VIa or VIb), m.p. 320° (corr.), $[\alpha]_D^{25} + 29.3^\circ \pm 1^\circ$ in CHCl₃. Reduction (Raney Ni, MeOH) of (IV) is described. H. W.

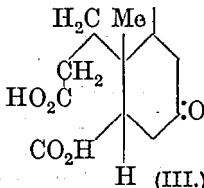
Location of oxygen in certain steroids. H. L. MASON and W. M. HOEHN (J. Amer. Chem. Soc., 1938, 60, 2566—2567).—3:12-Diketocholelate acid and Br in AcOH give the 4-*Br-acid*, m.p. 197—198° (decomp.), $[\alpha]_D^{25} + 109 \pm 2^\circ$ (*Me ester*, m.p. 200—201°, $[\alpha]_D^{25} + 170^\circ \pm 3^\circ$), converted by hot C₅H₅N into 3:12-diketo- Δ^4 -xiocholenic acid, m.p. 205—207°, $[\alpha]_D^{25} + 240^\circ \pm 5^\circ$ (*Me ester*, m.p. 235—237°, $[\alpha]_D^{25} + 242^\circ \pm 2^\circ$), differing from the acid obtained by oxidation of corticosterone, the indifferent O of which is thus not at C₍₁₂₎ (cf. Steiger *et al.*, A., 1938, II, 329). R. S. C.

Sulphonic acids of sterol derivatives. II. A. WINDAUS and K. H. MIELKE (Annalen, 1938, 536, 116—127; cf. A., 1937, II, 504).—*Me* coprostan-3-one-2-sulphonate (I), m.p. 282—283° [not m.p. 171—172° as recorded (*loc. cit.*)], is oxidised by CrO₃ in AcOH to the acid, C₂₇H₄₆O₄, m.p. 212—214° (not 201—202°), the constitution (*loc. cit.*) of which is

established by its conversion at 280—300°/13 mm. into the ketone (II), m.p. 106—107° (semicarbazone,



(II.)



(III.)

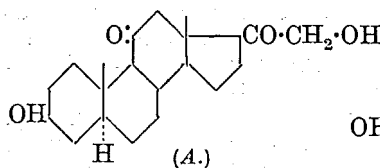
m.p. 245°, which gives the hydrocarbon, $C_{26}H_{46}$, m.p. 45—46°, identical with that described by Lettré (A., 1933, 1047). The mother-liquors from (I) contain much *Me coprostan-3-one-4-sulphonate*, m.p. 104—105°, oxidised to the dicarboxylic acid, $C_{27}H_{46}O_4$, m.p. 246° (Me_2 ester, m.p. 60°), obtained from coprosterol. Δ^5 -Cholestan-7-one-4-sulphonic acid (*loc. cit.*) is hydrogenated (Pd in EtOAc) to *cholestan-7-one-4-sulphonic acid*, m.p. 187° (*Me* ester, m.p. 133°; sparingly sol. alkali salts), which is oxidised (CrO_3 in 70% AcOH at 65°) to *cholestane-4:7-dione*, m.p. 146—147° (dihydropyridazine derivative, $C_{27}H_{44}N_2$, m.p. 167—169°), and the non-cryst. keto-acid (III) (*Me H* ester, m.p. 131°; *oxime*, m.p. 228°) identical with that obtained by Windaus (A., 1908, i, 728) from the Diels acid. Cholestane-3:6-dione is transformed by conc. H_2SO_4 - Ac_2O at -10° into non-cryst. *cholestane-3:6-dione-2-sulphonic acid*, the *Me* ester, m.p. 203—204°, of which is oxidised to the acid, $C_{27}H_{44}O_5$, m.p. 218—219°, obtained previously from the diketone; it is also obtained by the hydrogenation of Δ^4 -cholestene-3:6-dione-2-sulphonic acid (Pd-C in AcOH) whereby the position of SO_3H is established. *Me cholesterylenesulphonate* (*loc. cit.*) is reduced (Pd sponge in Et_2O) to *Me cholestane-6-sulphonate* (IV), m.p. 133° (with a non-identified, saturated ester, m.p. 97°), hydrolysed by LiOH to the somewhat sol. Li salt, which is oxidised by $KMnO_4$ to *cholestan-6-one*, m.p. 97—98°. (IV) is oxidised by fuming HNO_3 in AcOH at 100° to the acid, $C_{27}H_{46}O_4$, m.p. 271° (anhydride, m.p. 116—117°). Li cholesterylenesulphonate is oxidised ($KMnO_4$ in H_2O) to 4:5-dihydroxycholestan-3:6-dione, m.p. 219—224°. H. W.

Constituents of the adrenal cortex. XVIII. Hydrolysis of esters of reducing ketols by weak alkalis. T. REICHSTEIN and J. VON EUW (Helv. Chim. Acta, 1938, 21, 1181—1185; cf. A., 1938, II, 278).— $KHCO_3$ or, frequently, K_2CO_3 in H_2O -MeOH is suitable for the hydrolysis of esters derived from ketols with the group $:CR \cdot CO \cdot CH_2 \cdot OH$ ($R = H$ or OH). If only the primary OH at C_{21} is esterified treatment with $KHCO_3$ at room temp. for 24—48 hr. or for 1 hr. at the b.p. suffices for complete hydrolysis. If, also, Ac is present at C_{3} , reaction is not usually complete under these circumstances and somewhat more drastic conditions may be used without damaging the ketol group. The behaviour of the acetates of substance *Pa*, dehydro- and deoxy-corticosterone, and *trans*-dehydroandrosterone is described in detail.

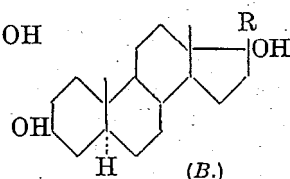
H. W.

Constituents of the adrenal cortex. XIX. Substances *N* and *P*. Configuration at C_{17} . T. REICHSTEIN and K. GÄTZI (Helv. Chim. Acta, 1938, 21, 1185—1196; cf. A., 1938, II, 278).—The

identity of substance *N* (I) with compound *H* (Kendall *et al.*, A., 1937, II, 459) is shown by direct comparison, by the identity of their diacetates, m.p. 148—149.5° (corr.), and by the stability of the latter towards CrO_3 -AcOH at room temp. (I) is therefore (*A*).



(A.)



(B.)

The reducing acetate, m.p. 210—211° (corr.) (*loc. cit.*; now regarded as *diacetate* of substance *P*; improved prep. described), is hydrolysed by $KHCO_3$ in boiling $MeOH$ - H_2O to substance *P* (*B*; $R = CO \cdot CH_2 \cdot OH$), m.p. 230—239° (corr.) (decomp.), $[\alpha]_D^{20} +48.0^\circ \pm 3^\circ$ in abs. EtOH, which readily reduces Ag_2O - NH_3 at room temp. and gives a ppt. with digitonin in hot 60% MeOH. This is converted by CrO_3 -AcOH at room temp. into androstane-3:17-dione and by HIO_4 into 3(β):17(β)-*dihydroxyalloethiocholanolic acid* (*B*; $R = CO_2H$), m.p. 277—278° (corr.; decomp.) [*Me* ester, m.p. 239—245° (decomp.); $[\alpha]_D^{21} +10.6^\circ \pm 2^\circ$ in MeOH]. Reduction (Raney Ni) of *P* gives substance *K* and the stereoisomeric *allopregnane-3(β):17(β):20:21-tetraol* (cf. *B*; $R = \begin{smallmatrix} CH_2 \cdot OH \\ | \\ H \cdot C \cdot OH \end{smallmatrix}$ and $\begin{smallmatrix} CH_2 \cdot OH \\ | \\ OH \cdot C \cdot H \end{smallmatrix}$),

m.p. 283—286° (corr.) when moderately rapidly heated [*triacetate*, m.p. 180—181° (corr.), $[\alpha]_D^{22} -1.3^\circ \pm 2^\circ$ in $COMe_2$].

All the pregnane derivatives obtained by addition of C_2H_2 or $MgEt$ halide to *trans*-androsterone or *trans*-dehydroandrosterone have the same configuration with respect to C_{17} , since they are all completely hydrogenated to *allopregnane-3:17-diol*. This is designated the 17(α)-series. Substance *K*, *P*, and the corresponding tetraol then belong to the 17(β) series. All known members of the 17(α) series do not give sparingly sol. ppts. with digitonin in 60% MeOH although OH at C_{3} is in the "cholestanol position." All known members of the 3(*trans*)-17- β -series give a ppt. under these conditions. H. W.

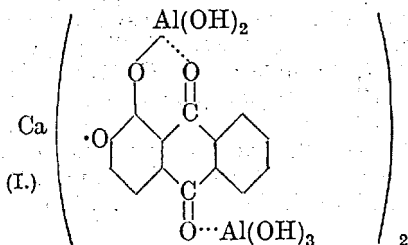
Constituents of the adrenal cortex. XX. Isolation of substances *Q* (deoxycorticosterone) and *R* and other compounds. T. REICHSTEIN and J. VON EUW (Helv. Chim. Acta, 1938, 21, 1197—1210).—Residues *A* II and *A* III (A., 1936, 1382) are freed as far as possible from corticosterone (I) and other substances by direct crystallisation from suitable solvents. The mother-liquors are treated with $KHCO_3$ -MeOH to hydrolyse possible esters and the neutral portions are treated with succinic anhydride and C_5H_5N for 16 hr. at room temp. The primary OH of ketol side-chains are nearly quantitatively esterified whilst *allopregnane* derivatives with *trans*-OH at C_{3} are partly acylated. The H succinates of the ketols are separated by their solubility in aq. Na_2CO_3 and hydrolysed ($KHCO_3$ -MeOH), giving greatly enriched ketol fractions from which considerable amounts of (I) are separated by crystallisation. The remaining amorphous residues are acetylated and chromatographed (Al_2O_3). The acetates of dehydrocorticosterone, (I), *Q* (deoxycorticosterone), *L*,

and *N*, 11-acetoxytrans-androsterone, and an acetate m.p. 240° (corr.), probably identical with that of *Fa*, are thus isolated with an acetate, m.p. 172—173° (corr.), of *R*, m.p. 202—204° (corr.); this reduces $\text{AgNO}_3\text{-NH}_3$ and presumably contains a ketol group.

H. W.

Indophenol reaction.—See A., 1938, I, 629.

Aluminium-calcium lake of alizarin. A. A. KRASNOVSKI (Prom. Org. Chim., 1938, 5, 597—604).—An adsorption complex of Ca^{++} and alizarin ion on



Al(OH)_3 is formed when aq. Na alizarate and CaCl_2 are added to an aq. suspension of Al(OH)_3 . The complex is changed to the compound (I) by boiling for 5 hr. An analogous product is obtained from purpurin-3-carboxylic acid.

R. T.

Derivatives of 1-aminoanthraquinone-2-carboxylamide.—See B., 1938, 1269.

Autoxidation of orcinol and *p*-xylorescinol [β -orcinol] in alkaline solution. F. HENRICH (Ber., 1938, 71, [B], 2049—2051; cf. A., 1915, i, 564).—

Exposure of solutions of β -orcinol in aq. KOH to air causes slow separation of a salt, $\text{C}_{16}\text{H}_{15}\text{O}_5\text{K}$, from which an *OH*-quinone (I) (apparently A), m.p. ~195—197° after softening at 185—195°, is obtained. It gives a triacetate, m.p. 145—148° after softening ~130°. (I) is reduced by SO_2 to the pentahydric phenol, $\text{C}_{16}\text{H}_{18}\text{O}_5$, m.p. 210—215°, becoming red (oxidation) at >190° (pentacetate, m.p. 192° after softening at 188—190°). Autoxidation in aq. NH_3 leads to different products.

H. W.

Diene syntheses starting from diphenylisobenzofuran. Synthesis of tetraphenylnaphthacene (rubrene). C. DUFRAISSE and P. COMPAGNON (Compt. rend., 1938, 207, 585—588; cf. A., 1938, II, 242).—A mixture of 1:2-diphenylisobenzofuran (I) and 1:4- $\text{O:C}_{10}\text{H}_6\text{:O}$ moistened with CHCl_3 affords 6:11-oxido-6:11-diphenyltetrahydronaphthacene-5:12-quinone, m.p. 155—157° (decomp.), dehydrated by cold H_2SO_4 (cf. A., 1938, II, 415) to 6:11-diphenylnaphthacene-5:12-quinone, which can be converted into rubrene. It has not been possible to dehydrate the adduct from (I) and $p\text{-O:C}_6\text{H}_4\text{:O}$.

J. L. D.

Anthranthrones and derivatives. III. Synthesis of substituted naphthastyrils. A. CORBELLINI and V. FOSSATI. IV. Synthesis of substituted anthranthrones. A. CORBELLINI, M. ATTI, and V. FOSSATI (R. Ist. lombardo Sci. Lett. Rend., 1936, [ii], 69, 258—272, 287—299; Chem. Zentr., 1936, ii, 4008).—III. 8-Hydroxymercuri-1-naphthoic

acid and its 3- and 4- NO_2 -derivatives [prep. from the appropriate naphthalic anhydride and Hg(OAc)_2 in aq. NaOH] with NaOHal give 8-bromo- (I), m.p. 172—173°, 8-iodo- (II), m.p. 164—165°, 8-bromo-3-nitro- (III), m.p. 237° (*Me*, m.p. 170°, and *Et*, m.p. 155°, esters; amide), and 8-bromo-4-nitro-1-naphthoic acid (IV), m.p. 203° (*Me*, m.p. 80—81°, and *Et*, m.p. 134°, esters; amide, m.p. 234—235°). Oxidation (KMnO_4) of (III) and (IV) gives 3-bromophthalic acid, m.p. 203° (anhydride, m.p. 132—133°). (I) and (II) with aq. 30% NH_3 at 150°, or in presence of Cu at ordinary pressure, give naphthastyril (V); (III), (IV), and 5:8:1- $\text{C}_{10}\text{H}_5\text{Br}_2\text{-CO}_2\text{H}$ similarly afford 6-nitro-, m.p. 256° (*Ac* derivative, m.p. 287°), 5-nitro-, m.p. 284° (*Ac* derivative, m.p. 236.5°), and 4-bromo-naphthastyril, m.p. 255—256°, respectively.

IV. Bromination of (V) gives its 4-Br-derivative, hydrolysed (10% NaOH) to 8:5:1- $\text{NH}_2\text{-C}_{10}\text{H}_5\text{Br-CO}_2\text{H}$, the cryst. diazo-compound of which with aq. $\text{NH}_3\text{-Cu}_2\text{O}$ affords 4:4'-dibromo-1:1'-dinaphthyl-8:8'-dicarboxylic acid (*Me*, ester, m.p. 206°, also by brominating *Me*, 1:1'-dinaphthyl-8:8'-dicarboxylate). 4-Chloronaphthastyril, m.p. 266° [from (V) and SO_2Cl_2 in AcOH], similarly yields 4:4'-dichloro-1:1'-dinaphthyl-8:8'-dicarboxylic acid (*Me*, ester, m.p. 206°), which is converted by conc. H_2SO_4 into 2:7-dichloroanthanthrone, m.p. >350° (cf. A., 1933, 1054); 4:9- and 3:8-dinitroanthanthrones, both m.p. >355°, are similarly obtained from 6:6'-, m.p. 326—327° (*Me*, ester, m.p. 290—293°), and 5:5'-dinitro-1:1'-dinaphthyl-8:8'-dicarboxylic acid, m.p. 320—325° (*Me*, ester, m.p. 259.5°), respectively. 4-Nitronaphthastyril, m.p. 297—298° [from (V) and AcOH-conc. HNO_3], is hydrolysed (5% NaOH) to 5-nitro-8-hydroxy-1-naphthoic acid, m.p. 243° (lactone, m.p. 248°; prep. by AcCl), and reduced (Sn, HCl) to 4-aminonaphthastyril, m.p. 244° (hydrochloride; *Ac* derivative, m.p. 283.5°) (decomp. of the diazonium salt gives no OH -derivative).

H. B.

Regularities of substitution in polynuclear vat dyes. III. 8:8'-Dibromoviolaanthrone. IV. Synthesis of 8:8'-dimethoxyviolaanthrone. T. MAKI and A. KIKUCHI (Ber., 1938, 71, [B], 2031—2036, 2036—2039; cf. A., 1937, II, 460).—III. Gradual addition of Br (1.5 mols.) to violaanthrone in conc. H_2SO_4 containing I at 100° gives mainly 8:8'-dibromoviolaanthrone (I) with small amounts of (?) 8:8'-dibromo-Bz-3:Bz-3'-dihydroxyviolaanthrone. A more highly brominated product loses Br when treated with alkaline $\text{Na}_2\text{S}_2\text{O}_4$, leaving nearly homogeneous (I). The constitution of (I) follows from the observation that it and the 8:8'-dimethoxy- (II) and 8:8'-diamino-violaanthrone derived from it give a red-violet vat whereas the corresponding Bz-3:Bz-3'- and Bz-2:Bz-2'-derivatives invariably give blue vats. (II) is a dark blue-violet vat dye whereas the corresponding indigo-blue Bz-3:Bz-3'- and the green Bz-2:Bz-2'-compounds are considerably lighter in shade. 8:8'-Dibromo-Bz-2:Bz-2'-dihydroxyviolaanthrone, obtained from (I) by oxidation with MnO_2 in conc. $\text{H}_2\text{SO}_4\text{-H}_3\text{BO}_3$, is readily converted by $p\text{-C}_6\text{H}_4\text{Me-SO}_3\text{Me}$ and Na_2CO_3 in $o\text{-C}_6\text{H}_4\text{Cl}_2$ into 8:8'-dibromo-Bz-2:Bz-2'-dimethoxyviolaanthrone. In

contrast, *Bz-3 : Bz-3'-dichloro-Bz-2 : Bz-2'-dihydroxyviolanthrone* is methylated with extreme difficulty in consequence of steric hindrance by the Cl atoms; the Br therefore are not attached to the *Bz* nuclei. (I) and the vat dyes derived therefrom are so readily and completely sol. in alkaline $\text{Na}_2\text{S}_2\text{O}_4$ that substitution cannot have occurred *ortho* to CO. 5 : 5'-Dimethoxyviolanthrone dissolves with difficulty. The shades on cotton given by (I) and related substances differ from those obtained with 6 : 6'-dibromoviolanthrone and its relations. (II) is oxidised by MnO_2 in conc. H_2SO_4 containing H_3BO_3 at 25° to *Bz-2-Bz-2'-dihydroxy-8 : 8'-dimethoxyviolanthrone*, which with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ and Na_2CO_3 in $o\text{-C}_6\text{H}_4\text{Cl}_2$ gives the corresponding *tetramethoxyviolanthrone* which is indifferent towards acids and alkalis.

IV. Gradual addition of 85% glycerol in 82% H_2SO_4 to a solution of 1-chloroanthraquinone and $(\text{NH}_2\text{Ph})_2\text{H}_2\text{SO}_4$ in 82% H_2SO_4 at 110° gives a mixture of 8-, m.p. 181.5° (corr.), 6-, m.p. $121\text{--}121.5^\circ$, and 11-chloro-, m.p. 151° (corr.), *benzanthrone-7* (III) (constitution established by its oxidation to 8-chloroanthraquinone-1-carboxylic acid). (III) is transformed by $\text{KOH}\text{--}\text{MeOH}$ at $150^\circ/13$ atm. mainly into 11-methoxybenzanthrone, m.p. 158.5° (corr.). This when added to a mixture of 81% KOH and PhOH at $190\text{--}210^\circ$ affords (II) and a more freely sol. dye.

H. W.

[Diene syntheses. XXIX. α -Terpinene.] K. ALDER (Ber., 1938, 71, [B], 2210—2211; cf. Diels *et al.*, A., 1938, II, 330).—The constitution ascribed by Wallach to α -terpinene has been confirmed already by Alder *et al.* (A., 1937, II, 345) and the course of its reaction with $(\text{C}\cdot\text{CO}_2\text{Et})_2$ has been elucidated.

H. W.

Hydrogen as carrier gas for the catalytic dehydrogenation of borneol to camphor. B. E. CHRISTENSEN, E. C. GILBERT, and M. BOCEK (J. Amer. Chem. Soc., 1938, 60, 2331—2333).—Spongy Cu, obtained by reducing fused CuO at 200° , gives a 96—100% yield of camphor from borneol (I) at 360° , but is rapidly deactivated and then not reactivated by H_2 . Use of H_2 as carrier for the (I) gives 96% yields at $320\text{--}480^\circ$ and no deactivation occurs. CO_2 gives quant. yields at $320\text{--}380^\circ$, but does not prevent deactivation. Ni and Co at $200\text{--}250^\circ$ give excellent yields and Co may be superior to Cu.

R. S. C.

Diterpenes. Phyllocladene and rimuene. C. W. BRANDT (New Zealand J. Sci. Tech., 1938, 20, 8B—15B).—Hydrogenation (Adams' catalyst) of phyllocladene (I) yields α -, m.p. 73° , $[\alpha]_D^{25} +23.9^\circ$ in CHCl_3 , and β -dihydrophyllocladene, m.p. $55\text{--}56^\circ$, $[\alpha]_D^{25} +12.5^\circ$ in CHCl_3 . With Se at 300° rimuene gives pimanthrene, and (I) yields small quantities of pimanthrene and retene, with traces of two hydrocarbons, a liquid (picrate, m.p. 144°) and a solid, m.p. 101° (picrate, m.p. 137°). (I) with 10% $\text{EtOH}\text{--}\text{H}_2\text{SO}_4$ or when regenerated from its hydrochloride gives isophyllocladene, m.p. 110° , enantiomorphous (?) with mirene. The constitution of these compounds is discussed.

A. Li.

Triterpene group. III. Double bond of β -boswellic acid. J. C. E. SIMPSON and N. E. WILLIAMS (J.C.S., 1938, 1712—1719).—Me *O*-acetyl- β -boswellate is not dehydrogenated by S and is recovered unchanged, but it contains $>\text{C}\cdot\text{CH}\cdot\text{C}\cdot$ (a). This compound is oxidised (CrO_3) to Me *O*-acetyl- β -boswellenonolate, m.p. $203\text{--}204^\circ$, $[\alpha]_D^{25} +51.7^\circ$, hydrolysed to Me β -boswellenonolate, m.p. $211\text{--}212^\circ$, $[\alpha]_D^{25} +120^\circ$, which is oxidised (CrO_3) to Me β -boswellendionate, m.p. $263.5\text{--}264^\circ$, $[\alpha]_D^{25} +117^\circ$, [monosemicarbazone, m.p. $280\text{--}281^\circ$ (decomp.)], also obtained by oxidation (KMnO_4) of Me β -boswellenonate. Nor- β -boswellanediolone, $\text{C}_{29}\text{H}_{46}\text{O}_2$ (cf. Simpson *et al.*, A., 1938, II, 287, formulated as $\text{C}_{26}\text{H}_{42}\text{O}_2$) is reduced [$\text{Pr}^i\text{OH}\text{--}\text{Al}(\text{OPr}^i)_3$] to nor- β -boswellanone, $\text{C}_{29}\text{H}_{48}\text{O}_2$, m.p. $231\text{--}232^\circ$, $[\alpha]_D^{25} +137^\circ$ (acetate, m.p. $236.5\text{--}238^\circ$, $[\alpha]_D^{25} +111^\circ$). Nor- β -boswellone is similarly reduced to nor- β -boswellenol, $\text{C}_{29}\text{H}_{48}\text{O}$, m.p. $190\text{--}191^\circ$, $[\alpha]_D^{25} +112^\circ$, of which the acetate, m.p. $165\text{--}166^\circ$, $[\alpha]_D^{25} +109^\circ$, is oxidised (KMnO_4) to a keto-acetate, m.p. $233\text{--}233.5^\circ$, $[\alpha]_D^{25} +163^\circ$, hydrolysed to the alcohol, $\text{C}_{29}\text{H}_{48}\text{O}_2$, m.p. $182\text{--}183^\circ$, $[\alpha]_D^{25} +159^\circ$; this is oxidised (CrO_3) to nor- β -boswellanediolone. $\text{C}_{29}\text{H}_{46}\text{O}_2$, m.p. $217\text{--}218^\circ$, $[\alpha]_D^{25} +159^\circ$ (azine, m.p. $210\text{--}211^\circ$; α -methyloxime, m.p. $199\text{--}200^\circ$), also obtained by oxidation (KMnO_4) of nor- β -boswellenone. Thus two types of oxidation involving the ethylenic linking of β -boswellic acid derivatives have been encountered:

(i) (a) $\rightarrow >\text{C}\cdot\text{CH}\cdot\text{CO}$, (ii) (a) $\rightarrow >\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot$. In any given ethylenic oxidation either (i) or (ii) occurs, but not both, the controlling factor being the degree of substitution of $\text{C}_{(1)}$. These selective oxidations suggest close association of $\text{C}_{(1)}\text{--}\text{C}_{(2)}$ with (a) and (b), such as would result from the presence of the double linking of β -boswellic acid at $\text{C}_{(6)}\text{--}\text{C}_{(7)}$ or $\text{C}_{(3)}\text{--}\text{C}_{(9)}$. All rotations are in CHCl_3 .

F. R. S.

Synthesis of esters of ursolic acid. H. M. SELL and R. E. KREMERS (J. Biol. Chem., 1938, 125, 451—453; cf. A., 1931, 491).—Acetylursolyl chloride (from the acid and SOCl_2), m.p. $200\text{--}201^\circ$, with various alcohols gives the following esters, having m.p. and $[\alpha]_D^{25}$ as shown: *Et*, 194° , $+60.8^\circ$; *Pr*, 173° , $+58.5^\circ$; *Bu*, $125\text{--}126^\circ$, $+54.5^\circ$; *n-amyl*, $110\text{--}111^\circ$, $+54.3^\circ$; *n-hexyl*, $123\text{--}124^\circ$, $+54.8^\circ$; *n-heptyl*, 93° , $+52.8^\circ$; *n-octyl*, 67° , $+51.5^\circ$.

A. Li.

Constituents of natural phenolic resins. XII. Action of selenium on lignans. J. R. ATKINSON and R. D. HAWORTH (J.C.S., 1938, 1681—1685).—Se-dehydrogenation of the Me_2 ether of olivil, isoolivil, lariciresinol, or isolariciresinol gives dehydroguaiaretic acid Me_2 ether and of *d*-pinoresinol Me_2 ether (I), *d*-epipinoresinol Me_2 ether, or *l*-eudesmin yields 2 : 5-diveratryl-3 : 4-dimethylfuran, m.p. $169\text{--}170^\circ$. This substance is obtained by the action of $\text{MeOH}\text{--}\text{HCl}$ on β -diveratroylbutane (II), m.p. $189\text{--}190^\circ$, prepared from β -bromopropioveratrone and Cu; this ketone could not be prepared by the action of I on the Na derivative on *Et* α -veratroylpropionate. The Se-dehydrogenation product confirms the C skeleton suggested for pinoresinol (III). Reduction ($\text{Na}\text{--}\text{EtOH}$).

of (II) gives $\alpha\delta$ -diveratryl- $\beta\gamma$ -dimethylbutane- $\alpha\delta$ -diol, b.p. 180—185°/1 mm., converted (MeOH-HCl) into 4-hydroxy-1-veratryl-6:7-dimethoxy-2:3-dimethyl-1:2:3:4-tetrahydronaphthalene, b.p. 178—182°/1 mm.; this transformation is analogous to the olivil-isoolivil change. Veratraldehyde and 1-keto-6:7-dimethoxy-3-methyl-1:2:3:4-tetrahydronaphthalene (HCl) give 1-keto-6:7-dimethoxy-2-veratrylidene-3-methyl-1:2:3:4-tetrahydronaphthalene, m.p. 146°, reduced (H_2 -Pd-C) to 1-keto-6:7-dimethoxy-2-(3':4'-dimethoxybenzyl)-3-methyl-1:2:3:4-tetrahydronaphthalene, m.p. 128—129°, which is further reduced (Zn-HCl) and dehydrogenated (Se) to 6:7-dimethoxy-2-(3':4'-dimethoxybenzyl)-3-methylnaphthalene, m.p. 115—116°. This substance is also obtained as an impurity in the product of Se-dehydrogenation of (I). F. R. S.

Egonol. II. Catalytic hydrogenation of acetylegonol and oxidative degradation of egonol by hydrogen peroxide. S. KAWAI and M. SUGA (Ber., 1938, 71, [B], 2071—2074; cf. A., 1938, II, 373).—Hydrogenation (PtO_2) of acetylegonol ceases after absorption of about 1 H_2 owing to inactivation of the catalyst if the usual proportion of the latter is used. With a very unusual proportion of the latter absorption proceeds much further and probably reaches finality after fixation of 7 H_2 . The isolation of homogeneous intermediate products appears impossible. Egonol (I) is oxidised by 30% H_2O_2 in AcOH at 80° to piperonylic and styrylic acid, (?) $OMe \cdot C_6H_3(OH) \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CO_2H$ (*Me styraxate*, m.p. 160—161°/0.05 mm.). The formulæ advanced previously (*loc. cit.*) for (I) are withdrawn.

H. W.

Are piperonyl groups present in lignins? K. KÜRSCHNER (Papier-Fabr., 1938, 36, 446—448; cf. B., 1934, 233; Hibbert *et al.*, A., 1938, II, 238).—Treatment of lignified tissue with EtOH- HNO_3 gradually removes the whole of the lignin (I) and the "nitrolignin" thus obtained does not give an appreciable amount of CH_2O when treated with acids. The groups which yield CH_2O do not appear to be present in (I) free from carbohydrates. The possibility that CH_2O_2 is affected by the nitration appears excluded by the observation that piperonal gives only minute amounts of CH_2O or CO_2 when treated with EtOH- HNO_3 . Piperonyl groups do not appear to be present in (I).

H. W.

Reactions involved in the sulphonation of heat-treated abietic acid. T. HASSELSTROM and J. D. McPHERSON (J. Amer. Chem. Soc., 1938, 60, 2340—2341).—Heat-treated abietic acid gives sulphohydroabietic acid, $C_{20}H_{28}O_5S$, + 3 H_2O (lost at 150°), m.p. 223—224° (decomp.) [Me_2 , m.p. 176.7—177.7° (corr.), and Et_2 ester, m.p. 150.4—151.4° (corr.); diamide, m.p. 254—255.5° (decomp.; corr.)]. The accompanying lactone (A., 1938, II, 288) is derived from a 10-OH-acid of the H_4 -series, thus confirming the disproportionation during heat-treatment.

R. S. C.

Melanoidin. C. ENDERS (Kolloid-Z., 1938, 85, 74—87).—A review of the literature. Analogies with humic acid are discussed. E. S. H.

Action of sodium cyanide on $\alpha\gamma$ -dibromo- $\alpha\gamma$ -dibenzoylpropane. R. C. FUSON, J. R. LITTLE, and G. MILLER (J. Amer. Chem. Soc., 1938, 60, 2404—2409).—Br converts $CH_2(CH_2Bz)_2$ into forms, (I), m.p. 117—118°, (II), m.p. 112—113°, and m.p. 90—94° (Conant *et al.*, A., 1927, 522, m.p. 89°); admixture with (I) depresses the m.p. of (II), and Conant's form, m.p. 115—115.5°, was probably a mixture. With NaCN in 90% EtOH (III) gives forms, (A), m.p. 166—167° (52—68%), (B), m.p. 101—102° (12—16%), (C), m.p. 86—88° (0—2%), and (D), m.p. 120—123° (about 6%), of 3-bromo-2-cyano-5-benzoyl-2-phenyltetrahydrofuran. With KCN in abs. EtOH (III) gives only a halogenated compound, m.p. 127—128.5°. (A), (B), (C), and (D) gives oximes, m.p. 171—173°, 179—181°, 182—183°, and 180—182°, respectively. (A), (B), and (D) give semicarbazones, m.p. 202°, 178—179°, and 202°, respectively. With HCl-AcOH at 100° (A) gives 3-bromo-5-benzoyl-2-phenyltetrahydro-2-furoamide, m.p. 200—201°, also obtained from (A) by HCl-MeOH with much *Me* 3-bromo-5-benzoyl-2-phenyltetrahydro-2-furoate, m.p. 101—102° (converted by NH_3 into the amide), and from (B) [(?) (D)] by dry HCl-MeOH (no ester formed). With NaOH in aq. MeOH or, less well, KCN or NaOAc (A), (B), (C), and (D) lose 1HBr and yield 2-cyano-2-benzoyl-2-phenyl-2:5-dihydrofuran (IV), m.p. 136—137° (decomp. from 130°), enolisation at the $CO \cdot CH_{1.5}$, causing disappearance of the isomerism. A similar enolisation accounts for spontaneous change of (C) into (B). With hot, conc. HCl (IV) undergoes hydrolysis of the CN, ring-fission, ring-closure, and dehydration, giving as final product 6-benzoyl-3-phenyl-1:2-pyrone, m.p. 126—127° (oximes, m.p. 193—194° and 159—161°), which is hydrogenated (PtO_2) in $OH \cdot [CH_2]_2 \cdot O \cdot [CH_2]_2 \cdot OMe$ to δ -benzoyl- α -phenyl- δ -valerolactone, m.p. 142—143°, and (?) 3-phenyl-6- α -hydroxybenzyl-1:2-pyrone, m.p. 137—138° (acetate, m.p. 102—103°), and is converted by O_3 in AcOH, followed by H_2 -Pd, into $(CHO)_2$ and $BrCO_2H$. The ring-closure of (I) by NaCN probably occurs by addition of CN^- , followed by elimination of Br^- ; this and similar ring-closure (*e.g.*, formation of epoxynitriles) demand the presence of H_2O , that the halogen atom reacting shall be in the α -position to a CO or Ph, that the CO reacting shall have a halogen in the α -position to it, and that steric relations shall be favourable, but these conditions alone do not always suffice, *e.g.*, $(CH_2 \cdot CHBzBr)_2$ gives a dihydropyrone. R. S. C.

New method for the isolation of α - and β -tocopherols. A. R. MOSS and J. C. DRUMMOND (Biochem. J., 1938, 32, 1953—1956).—Chromatographic adsorption of wheat-germ oil from light petroleum on Al_2O_3 yields oils, which after hydrolysis and treatment with $NH_2 \cdot CO \cdot NH \cdot COCl$ give α - and β -tocopherol allophanate. From ultra-violet absorption spectra of the adsorbed oils before and after "allophanation," it is probable that α - (I) and β -tocopherol contain free OH, the hydrolysis stage in the isolation merely removing saponifiable material. (I) shows slight optical activity and it is probable that

it is optically active in the original oil, partial racemisation taking place during the hydrolysis. J. D. R.

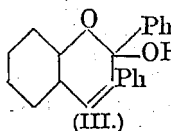
Coumarin-3-carboxylamides.—See B., 1938, 1365.

Condensation of α -substituted acetoacetic esters with phenols. I. Pechmann reaction with ethyl α -acetylglutarate. N. M. SHAH and R. C. SHAH (Ber., 1938, 71, [B], 2075—2081).—Condensation with $\text{Et}_2\alpha$ -acetylglutarate (I) occurs best with *meta*-substituted phenols and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$. It does not occur with PhOH , *o*-cresol, $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, *o*- and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$, resacetophenone, β -resorcylic or gallic acid. *p*-Cresol gives unsatisfactory yields. Slow addition of conc. H_2SO_4 to (I) and *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ at 0° gives 7-hydroxy-4-methylcoumarin-3-propionic acid (II), m.p. 224° (*Ca* and *Ag* salts; *Ac* derivative, m.p. $195\text{--}196^\circ$; *Me* ether, m.p. $172\text{--}173^\circ$), and *Et* 7-hydroxy-4-methylcoumarin-3-propionate, m.p. 124° (*Ac*, m.p. 113° , and *Bz*, m.p. 84° , derivatives). NaOH and Me_2SO_4 transform (II) into 2:4-dimethoxy- β -methyl- α - β' -carboxyethylcinnamic acid, m.p. $152\text{--}153^\circ$ (*Ca* and *Ba* salts). 1:2:3- $\text{C}_6\text{H}_3(\text{OH})_3$ and (I) give 7:8-dihydroxy-4-methylcoumarin-3-propionic acid (+ H_2O) (*Ac* derivative, m.p. 182° ; *Me*, m.p. $207\text{--}208^\circ$, and *Et*, m.p. 157° , ester), converted by KOH and Me_2SO_4 into 2:3:4-trimethoxy- β -methyl- α - β' -carboxyethylcinnamic acid, m.p. $146\text{--}147^\circ$. $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$ and (I) give *Et* 4-methyl-1-naphthopyrone-3-propionate, m.p. 155° , hydrolysed to 4-methyl-1-naphthopyrone-3-propionic acid, m.p. 230° (*Ag* and *Ca* salts). Phloroglucinol, (I), and conc. H_2SO_4 at 0° afford 5:7-dihydroxy-4-methylcoumarin-3-propionic acid, m.p. $257\text{--}258^\circ$ (decomp.). 5-Hydroxy-4:7-dimethylcoumarin-3-propionic acid, m.p. $258\text{--}260^\circ$, and its *Et* ester, m.p. 165° , are derived from orcinol. *m*-Cresol gives 4:7-dimethylcoumarin-3-propionic acid, m.p. $160\text{--}162^\circ$ (*Ca* and *Ag* salts; *Et* ester, m.p. $83\cdot5^\circ$), whilst 4:6-dimethylcoumarin-3-propionic acid, m.p. $176\text{--}178^\circ$ (*Ag* salt), is derived from *p*-cresol. H. W.

Constitution of oroxylin-A. II. Attempted synthesis of oroxylin-A and the synthesis of wogonin. R. C. SHAH, C. R. MEHTA, and T. S. WHEELER (J.C.S., 1938, 1555—1559).—Baicalein, sitosterol, and galactose have been isolated from the root-bark of *Oroxylum indicum*, Vent. 2:4-Dihydroxy-3:6-dimethoxyacetophenone (I), Bz_2O , and NaOBz give 7-hydroxy-5:8-dimethoxyflavone (II), m.p. $287\text{--}288^\circ$, which is methylated to 5:7:8-trimethoxyflavone, m.p. $167\text{--}168^\circ$, also obtained by methylation of wogonin (III). Demethylation of (II) with HI gives 5:6:7-trihydroxyflavone (baicalein) and with AlCl_3 5:7:8-trihydroxyflavone, m.p. $250\text{--}251^\circ$, not identical with baicalein. Partial demethylation of (II) with AlCl_3 gives (III); that of (I) leads to 2:4:6-trihydroxy-3-methoxyacetophenone, m.p. 188° . F. R. S.

Condensation of salicylaldehyde and deoxybenzoin. P. P. HOFF and R. J. W. LE FÈVRE (J.C.S., 1938, 1582—1584).—*o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (I), CH_2PhBz (II), and dry HCl in MeOH , EtOH , Et_2O , AcOH , EtOAc , or 99% HCO_2H , at $0\text{--}30^\circ$, afford 2:3-diphenylbenzopyrylium chloride, m.p. $\sim 200^\circ$ (cf. Das and Ghosh, J.C.S., 1919, 115, 817) [ferri-

chloride, m.p. 124° (cf. Decker *et al.*, A., 1909, i, 116)], which gives the pyranol (III), m.p. 124° (picrate, decomp. $\sim 235^\circ$), best purified by diluting an AcOH solution of the perchlorate, m.p. 246° (darkens at 240°), prepared from aq. HClO_4 and (II), or better from



(I), (II), anhyd. Et_2O , HClO_4 , and dry HCl at 0° . (I) and (II) do not react in aq. $\text{KOH}\text{--}\text{EtOH}$. (I), (II), EtOH and piperidine at room temp. give (III) and not salicylidenedeoxybenzoin (cf. Singh *et al.*, J.C.S., 1919, 115, 821; Hill, A., 1936, 997), confirmed by chemical properties and by physical measurements, *e.g.*, effect on dielectric const., d , and η of C_6H_6 , under comparable conditions of temp. and concn., and calculation of dipole moments. A. T. P.

Natural flavones. II. Colouring matters of the bark of *Oroxylum indicum*, Vent.—See A., 1938, III, 1066.

Flavone glucosides.—See B., 1938, 1363.

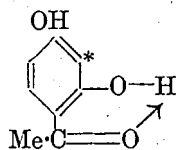
Dehydrogenation by organometallic compounds. H. GILMAN and C. W. BRADLEY (J. Amer. Chem. Soc., 1938, 60, 2333—2336).—1:4-Dihydrodibenzfuran (I) [prepared from dibenzfuran (II) by Na in liquid NH_3], m.p. 42° , b.p. $110^\circ/5\text{ mm.}$, with LiPh in boiling Et_2O gives 70% of pure (II), 19% of C_6H_6 , and LiH . Metallation for a shorter period, followed by treatment with CO_2 , gives 3:4-dihydrodibenzfuran-3-carboxylic acid, m.p. $278\text{--}279^\circ$, converted by S at 250° into dibenzfuran-3-carboxylic acid. LiBu^α and NaBu^α also effect this dehydrogenation. 1:4-Dihydronaphthalene and LiPh give C_{10}H_8 more slowly or, by CO_2 , 1:2-dihydro-2-naphthoic acid. Carboxylation involves an allylic rearrangement, the Li entering (I) at $\text{C}_{(1)}$, ($\text{:CH}\cdot\text{CH}_2\text{Ph}$) $_2$ and LiBu^α give similarly 12—15% of ($\text{:CH}\cdot\text{CHPh}$) $_2$ and 12% of ($\text{:CH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$) $_2$. R. S. C.

Mercuric halide dioxanates.—See A., 1938, I, 622.

2-Hydroxymethyl-1:3-dioxacyclopentane.—See B., 1938, 1270.

Aluminium chloride, a new reagent for the condensation of β -ketonic esters with phenols. III. Condensation of phenolic ketones with ethyl acetoacetate. N. M. SHAH and R. C. SHAH (J.C.S., 1938, 1424—1428).—Orcacetophenone (I) and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ (II), when heated with $\text{AlCl}_3\text{--PhNO}_2$ ($110\text{--}115^\circ$ and finally 150°), afford 5-hydroxy-(III) and 5-hydroxy-6-acetyl-, m.p. 180° , -4:7-dimethylcoumarin (*Ac* derivative, m.p. $149\text{--}150^\circ$), also obtained when the *Ac* derivative of the former is heated with AlCl_3 ($170\text{--}180^\circ$; 2.5 hr.; Fries), and converted by $\text{Ac}_2\text{O}\text{--}\text{NaOAc}$ at $160\text{--}170^\circ$ (8—9 hr.) into 3'-acetyl-4:2':5-trimethylchromono-(7':8':6:5)- α -pyrone, m.p. $275\text{--}276^\circ$. Condensation of (I) and (II) in presence of H_2SO_4 gives (III); H_2SO_4 acting on (I) gave indications of the elimination of *Ac* with the formation of orcinol. By similar methods 2:4-dihydroxybenzophenone and (II) give 5-hydroxy-6-benzoyl-4-methylcoumarin, m.p. $184\text{--}185^\circ$ (*Ac*, m.p. 150° , and *Bz*, m.p. $199\text{--}200^\circ$, derivatives), also obtained by Fries transformation of 5-benzoyloxy-4-

methylcoumarin, and converted by $\text{Ac}_2\text{O}-\text{NaOAc}$ (170—180°; 11 hr.) into 4'-phenyl-4-methylcoumarino-(7':8':6:5)- α -pyrone + $0.25\text{H}_2\text{O}$, m.p. 220—221°. 2-Acetylresorcinol and (II) with $\text{AlCl}_3-\text{PhNO}_2$ at 125—135° or H_2SO_4 afford 7-hydroxy-8-acetyl-4-methylcoumarin (IV). Clemmensen reduction of the O-Me derivative of (IV) affords 7-methoxy-4-methyl-8-ethylcoumarin, m.p. 133—134°. Similarly phloracetophenone and (II) give 5:7-dihydroxy-6(or 8)-acetyl-4-methylcoumarin, m.p. 286—287° (Me_2 ether, m.p. 165—166°), the latter being the more probable owing to the ease of methylation. Gall-, quin-, and o-hydroxy-acetophenone do not condense with (II) in presence of either AlCl_3 or H_2SO_4 . A mechanism is

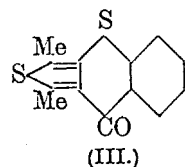


proposed to account for the course of the foregoing reactions, involving the stabilisation of one of the Kekulé forms by the fixation of the double bonds owing to the formation of a chelate ring (cf. annexed formula); condensation then only occurs at C* when, as shown, this is doubly linked to a C bearing another OH. H. G. M.

Compound from *Derris elliptica* resin. S. H. HARPER (Chem. and Ind., 1938, 1059).—By chromatography this resin yields the substance, m.p. 180° (Buckley, B., 1936, 1117), which is $\text{C}_{20}\text{H}_{16}\text{O}_6$ (formula suggested). R. S. C.

3:4-Dehydrocyclotetramethylene sulphone.—See B., 1938, 1268.

Thiophen series. XLIII. Derivatives of 2:5-thioxen. W. STEINKOPF, I. POULSSON, and O. HERDEY (Annalen, 1938, 536, 128—134).—Gradual addition of powdered I to 2:5-dimethylthiophen and yellow HgO at $\geq 50^\circ$ gives 3-iodo-2:5-dimethylthiophen (I), b.p. 99—100°/11.5 mm. (yield 58%), transformed by the successive action of MgEtBr and CO_2 into 2:5-dimethylthiophen-3-carboxylic acid, m.p. 115°. Analogously 3:4-di-iodo-2:5-dimethylthiophen (II) affords 4-iodo-2:5-dimethylthiophen-3-carboxylic acid, m.p. 199°. Anhyd. K_2CO_3 , $\text{Cu}(\text{OAc})_2$, $o\text{-SH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and (I) in amyl alcohol at 130—140° yield 3-o-carboxyphenylthiol-2:5-dimethylthiophen, m.p. 198—199.5°, converted by conc. H_2SO_4 at 85° into 2:5-dimethylthiophen-3:4-thiochromone [2':5'-dimethylthiopheno-(3':4'-2:3)-benz-1:4-thiopyrone] (III), m.p. 104—105°, which is intensely yellow and gives an intensely red-violet, non-fluorescent solution in conc. H_2SO_4 ; it is also obtained from the acid and PCl_5 in C_6H_6 . (II) and $o\text{-SH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ afford 3:4-di-o-carboxyphenylthiol-2:5-dimethylthiophen, decomp. $>295^\circ$.



Addition of AlCl_3 to 2:5-dimethylthiophen and $(\text{CH}_3\text{CO})_2\text{O}$ in PhNO_2 at 0—5° yields γ -keto- γ -3-2:5-dimethylthiophenyl-n-butyric acid, m.p. 111—112°, reduced (Clemmensen) to γ -3-2:5-dimethylthiophenyl-n-butyric acid, m.p. 55—56°, cyclised by conc. H_2SO_4 at 85° to 3-keto-2:7-dimethyl-3:4:5:6-tetrahydro- β -thionaphthen [3'-keto-2:5-dimethyl-3':4':5':6'-tetrahydrobenz-(1':2'-3:4)-thiophen], m.p. 39.5—41°, which slowly decomposes on exposure to air; this is reduced (Clemmensen)

to 2:7-dimethyl-3:4:5:6-tetrahydro- β -thionaphthen [2:5-dimethyl-3':4':5':6'-tetrahydrobenz-(1':2'-3:4)-thiophen], b.p. 245°. 3:4-Dinitro-2:5-dimethylthiophen, m.p. 118—119°, obtained by means of KNO_3 and H_2SO_4 , is transformed by fuming HNO_3 into 3:4-dinitro-5-methyl-2-thienyl nitrate, m.p. 83.5—85°, transformed by an excess of Br and a trace of I at 150° into tetrabromothiophen, m.p. 114.5—115.5°. H. W.

Thiophen series. XLIV. Bromo- and chloro-derivatives of 3-thiotolen. W. STEINKOPF and W. NITSCHKE (Annalen, 1938, 536, 135—142).—Partly a revision of previous work (Steinkopf *et al.*, A., 1935, 354; 1937, 11, 514; Rinkes, A., 1935, 221). Et 3-methylthiophen-2-carboxylate is treated with $\text{Br}-\text{H}_2\text{O}$ and the product is hydrolysed to 4-bromo-3-methylthiophen-2-carboxylic acid, m.p. 187.5—188.5° (Me ester, m.p. 61—61.5°); this is converted by yellow HgO in boiling AcOH into 4-bromo-2:5-diacetoxymercuri-3-methylthiophen, m.p. $>320^\circ$ after darkening at about 250°, transformed by boiling aq. NaCl into 4-bromo-2:5-dichloromercuri-3-methylthiophen and thence by distillation with HCl into 4-bromo-3-methylthiophen, b.p. 179—181°. Similarly 4:5-dibromo-3-methylthiophen-2-carboxylic acid is converted successively into 4:5-dibromo-2-acetoxymercuri-3-methylthiophen, the corresponding 2-chloromercuri-derivative, and 4:5-dibromo-3-methylthiophen, b.p. 109.5—111°/14.5 mm., 234.5—235.5°/atm. pressure. This is converted by successive treatments with MgEtBr and CO_2 into 4-bromo-3-methylthiophen-5-carboxylic acid, m.p. 225—225.5° (Me ester, b.p. 140.5°/12 mm., m.p. 77.5—78°), brominated to Me 2:4-dibromo-3-methylthiophen-5-carboxylate, m.p. 89—90° (corresponding acid, m.p. 216—217°). 2:4-Dibromo-3-methylthiophen, b.p. 105°/13.5 mm., obtained from the acid in the usual manner, is transformed by $\text{HgCl}_2-\text{NaOAc}$ into 2:4-dibromo-5-chloromercuri-3-methylthiophen, m.p. 208—209°. Passage of Cl_2 through a solution of Me 4:5-dibromo-3-methylthiophen-2-carboxylate in boiling AcOH affords Me 4:5-dichloro-3-bromomethylthiophen-2-carboxylate (I), m.p. 61.5—62.5°, converted by boiling 10% KOH into 4:5-dichloro-3-hydroxymethylthiophen-2-carboxylic acid; the corresponding Me ester, m.p. 87.5—88.5°, is reconverted into (I) by PBr_3 in CHCl_3 at room temp. Passage of Cl_2 through a well-cooled solution of Me 3-methylthiophen-2-carboxylate in CS_2 gives 4:5:x:y-tetrachloro-3-methyltetrahydrothiophen, m.p. 52.5—53.5°, converted by 20% $\text{KOH}-\text{EtOH}$ into 4:5-dichloro-3-methylthiophen-2-carboxylic acid, m.p. 197—197.5° (Me ester, m.p. 83.5—84°). This is transformed into 4:5-dichloro-3-methylthiophen, b.p. 96.5°/31 mm., whence 4:5-dichloro-2-chloromercuri-3-methylthiophen, m.p. 230.5—231°. H. W.

Highly arylated compounds. VII. Derivatives of tetraphenylthiophen. W. DILTHEY, E. GRAEF, H. DIERICH, and W. JOSTEN (J. pr. Chem., 1938, [iii], 151, 185—190).—2:5-Diphenyl-3:4-diphenylenethiophen (I) and S in boiling PhCl slowly afford the compound, $\text{C}_{29}\text{H}_{18}\text{OS}_{4.5}$, m.p. 295—296°, or m.p. 298—299° when placed in a bath preheated to 290°, which passes at 320° into CO_2 , (?) COS , and 2:5-diphenyl-3:4-diphenylenethiophen [2:5-diphenylphenanthreno-(9':10'-3:4)thiophen], m.p. 204°, also ob-

tained directly from (I) and S in CO_2 at 290–320°. The colourless compound gives an orange-red solution in conc. H_2SO_4 . 3:4:5-Triphenyl-2-*p*-anisylcyclopentadienone and S at 290–320° yield 3:4:5-triphenyl-2-*p*-anisylthiophen, m.p. 161°, which shows yellow halochromism in conc. H_2SO_4 ; it is oxidised by 30% H_2O_2 in boiling AcOH to the corresponding sulphone, m.p. 237°.

H. W.

β -Substituted hydroxylamines. IV. Action of phenylhydroxylamine on compounds with an ethylenic linking. E. JOLLES (Gazzetta, 1938, 68, 488–496).—*trans*-Dibenzoyl ethylene and $\text{NHPH}\cdot\text{OH}$ (I) or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{OH}$ (II) form *anilino*-, m.p. 128°, or *p*-toluidino-dibenzoyl ethylene, m.p. 142°. From $\text{COPh}\cdot\text{CH}\cdot\text{CHPh}$, β -phenyl-, m.p. 149–150°, and β -*p*-tolyl-hydroxylamino- β -phenylpropionophenone, m.p. 151°, are obtained. Maleimide and (II) give 3-*p*-tolylhydroxylamino-2:5-diketopyrrolidine, m.p. 185° (decomp.), which when heated in $\text{C}_5\text{H}_5\text{N}$ forms 3-*p*-toluidino-2:5-diketopyrroline, m.p. 224°. 3- α -Naphthylhydroxylamino-2:5-diketopyrrolidine, m.p. 166°, is prepared similarly. $\text{CHPh}\cdot\text{C}(\text{CO}_2\text{Et})_2$ and benzylidenemalon dianilide, m.p. 247°, with (I) give Et_2 (phenylhydrazinobenzyl)malonate, m.p. 110–112°, and the corresponding malondianilide, m.p. 284°, respectively. Benzylidenecamphor, cinnamanilide, Et crotonate, and $\text{CHPh}\cdot\text{N}\cdot\text{NHPH}$ do not react with (I). Benzylidene-1-phenyl-3-methylpyrazolone and (I) yield an additive product, m.p. 110°; when heated in EtOH they form the benzylidenedipyrazolone, and in $\text{C}_5\text{H}_5\text{N}$ the dipyrazolone, with a product, m.p. 100°. Benzylidene- and *p*-hydroxybenzylidene-aniline and (I) form diphenyl- and phenyl *p*-hydroxyphenyl-nitrone, m.p. 210°, respectively.

E. W. W.

Effect of chemical structure on local anaesthetic action of diothane analogues. (Miss) E. M. WALTER (J. Amer. Chem. Soc., 1938, 60, 2467–2469).— α -Piperidinopropane- β -diol dibenzoate hydrochloride (I), m.p. 126–130°, difuroate, m.p. 73–74° (hydrochloride, m.p. 163–164.5°), diacetate (II) hydrochloride, m.p. 128–133°, dicinnamate hydrochloride, m.p. 159–161°, and di-(2-furylacrylate), an oil (hydrochloride, an oil), are prepared. All except (II) have anaesthetic action, furyl increasing the stability and decreasing the irritation compared with (I).

R. S. C.

Development of pyridine chemistry. VON SCHICKH (Angew. Chem., 1938, 51, 779–783).

Pyridine derivatives.—See B., 1938, 1270.

Derivatives of 3:5-di-iodo-4-pyridone-2:6-dicarboxylic acid. M. HEROLD, E. JIRÁT, and A. ZUBENKO (Časopis českoslov. Lék., 1936, 16, 210–214; Chem. Zentr., 1937, i, 2371).— Me_2 3:5-di-iodo-4-pyridone-2:6-dicarboxylate (I) and $\text{MeI} + \text{Ag}$ in xylene at 160° or $\text{Me}_2\text{SO}_4 + \text{MgO}$ in xylene at 100° give the *N*-Me derivative, m.p. 195–196°, hydrolysed to 3:5-di-iodo-*N*-methyl-4-pyridone-2:6-dicarboxylic acid, m.p. 175° (Et_2 , m.p. 112.5°, and Pr_2 , m.p. 74.5–75.5°, esters). Me_2 3:5-di-iodo-4-methoxy-, m.p. ~125° [from (I) and $\text{Et}_2\text{O}\cdot\text{CH}_3\text{N}_2$ or $\text{MeI}\cdot\text{Ag}_2\text{O}$ in xylene at 110°], 4-ethoxy-, m.p. 130°, and 4-propoxy-, m.p. 89°, pyridine-2:6-dicarboxylates are described; the free acids have m.p. 176°, 173°, and 155°, respectively.

H. B.

Synthesis of polycyclic indoles. G. BARGER and (Miss) E. DYER (J. Amer. Chem. Soc., 1938, 60, 2414–2416).—1-Amino-1:2:3:4-tetrahydroquinoline [modified prep.; *picrate*, m.p. 140–141° (decomp.)] and the appropriate CO-compound give 1-carboxymethylene- (I), m.p. 98–99°, 1- α -phenylethylidene- (II), m.p. 84.5–85.5°, and 1-isopropylidene-amino-1:2:3:4-tetrahydroquinoline (III), b.p. 153°/12 mm. (*picrate*, m.p. 138–140°). With 10% HCl at 55° (I) gives 1:7-trimethyleneindole-2-carboxylic acid, m.p. 210–212° (decomp.), converted by $\text{Cu}\cdot\text{Cr}_2\text{O}_3$ in quinoline- H_2 at 180–190° into 1:7-trimethyleneindole, m.p. 86.5–88° (*picrate*, m.p. 138–139°), which is not identical with a compound obtained (unpublished) from calycanthine, but is reduced by Zn dust and HCl to 1:7-trimethylene-2:3-dihydroindole [lilolidine], b.p. about 140°/12 mm. [*picrate*, m.p. 168–178° (von Braun, A., 1918, i, 40, m.p. 138°)]. With anhyd. ZnCl_2 at 120° (II) gives 22% of 2-phenyl-1:7-trimethyleneindole, m.p. 133–134°. 1-Amino-1:2:3:4-tetrahydro-5:6-benzoquinoline, m.p. 107–108° [sulphate, +4 H_2O , m.p. 182° (decomp.)], gives 1-carboxymethyleneamino-1:2:3:4-tetrahydro-5:6-benzoquinoline, m.p. 122–123°; this did not undergo indole ring-closure, which failed also with (III) and 1-carboxymethyleneaminocarbazole, m.p. 148–150° (decomp.).

R. S. C.

Catalytic reduction of *o*-nitrocinnamionitriles. K. H. BAUER (Ber., 1938, 71, [B], 2220–2229).—Reduction (H_2 -Pd-SiO₂ in EtOH) of *o*-nitro- α -phenylcinnamionitrile gives 2-amino-3-phenylquinoline 1-oxide, $\text{C}_6\text{H}_4\text{CH}(\text{CPh})\text{NO}\cdot\text{C}\cdot\text{NH}_2$ or $\text{C}_6\text{H}_4\text{CH}(\text{CPh})\text{N}(\text{OH})\cdot\text{C}\cdot\text{NH}_2$, m.p. 184–185°, which gives a dark blue colour with FeCl_3 in EtOH and is reduced by Fe powder and AcOH or by H_2SO_3 at 120° to 2-amino-3-phenylquinoline, m.p. 156°. Similarly Et *o*-nitro- α -cyanocinnamate is reduced to 2-amino-3-carbethoxyquinoline 1-oxide, m.p. 141–142° (complex Ni derivative), converted by Fe powder and AcOH into Et 2-aminoquinoline-3-carboxylate, m.p. 135°, also obtained by H_2SO_3 at 120°. It is hydrolysed to 2-aminoquinoline-3-carboxylic acid (NH_4 salt).

H. W.

8-Quinolyl benzyl- and hydr-oxyethyl ether.—See B., 1938, 1268.

isoQuinoline derivatives.—See B., 1938, 1365.

Sterol hydantoins.—See B., 1938, 1366.

Racemisation of tripeptides and hydantoins. M. BOVARNICK and H. T. CLARKE (J. Amer. Chem. Soc., 1938, 60, 2426–2430).—Racemisation of acyl-amidoacylanilides and hydantoins is not due to formation of conjugated ethylenic linkings, since it is not prevented by appropriate substitution. Substitution sometimes increases the rate of racemisation, which is thus probably dependent on electronic effects. Carbobenzyl-oxy-*p*-anisylalanine, m.p. 106–107°, $[\alpha]_D^{25} +12^\circ$ in 95% EtOH, is prepared and thence *N*-carbobenzyl-oxy-*p*-anisylalanylalanilide, m.p. 171–173°, $[\alpha]_D^{25} +22.3^\circ$ in COMe_2 , and *p*-anisylalanylalanilide (I), m.p. 121–123°, $[\alpha]_D^{25} +34.3^\circ$ in 95% EtOH (*N*-Ac, m.p. 168–170°, $[\alpha]_D^{25} +56.4^\circ$ in 95% EtOH, and *N*-Bz derivative, m.p. 224–225°, $[\alpha]_D^{25} +14.7^\circ$

in COMe_2). $\text{HI-Ph}_4\text{I}$ at room temp. converts (I) into *tyrosylanilide*, m.p. 145—147°, $[\alpha]_D^{25} +28.4^\circ$ in 95% EtOH (*Ac* derivative, m.p. 236—237°, $[\alpha]_D^{25} +61.0^\circ$ in 95% EtOH). *N-p-Toluenesulphonyl-p-anisylalanine*, m.p. 138—140°, with PCl_5 in Et_2O , followed by NHPhMe , gives *p-toluenesulphonyl-p-anisylalanylmethylanilide*, m.p. 120°, $[\alpha]_D^{25} +18.8^\circ$ in 95% EtOH, and another substance. *N-p-Toluenesulphonyl-ON-dimethyltyrosine* with PCl_5 and then NH_2Ph gives *N-p-toluenesulphonyl-N-methyl-p-anisylalanylanilide*, m.p. 96—98°, $[\alpha]_D^{25} +15.3^\circ$ in 95% EtOH, converted by $\text{HI-Ph}_4\text{I}$ at room temp. into *methyltyrosylanilide*, m.p. 139—140°, $[\alpha]_D^{25} +46.8^\circ$ in 95% EtOH (*Ac* derivative, m.p. 185—186°, $[\alpha]_D^{25} -32.1^\circ$ in 95% EtOH). *N-Methyltyrosine* with KCNO gives *5-p-hydroxybenzyl-1-methylhydantoin*, m.p. 123—124°, $[\alpha]_D^{25} -12.0^\circ$ in 95% EtOH, and with PhNCO *3-phenyl-5-p-hydroxybenzyl-1-methylhydantoin*, m.p. 153—155°, $[\alpha]_D^{25} -15.5^\circ$ in 95% EtOH. *p-Anisylalanine* gives *5-p-methoxybenzylhydantoin*, m.p. 171—173°, $[\alpha]_D^{25} -89.0^\circ$ in 95% EtOH. Rates of racemisation of 13 of the above compounds are recorded.

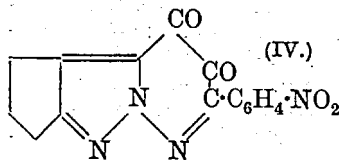
R. S. C.

Reaction between mercury fulminate and some pyrazole derivatives. G. Losco (Gazzetta, 1938, 68, 474—480).—1-Phenyl-3-methyl-5-pyrazolone with the additive compound $\text{Hg}(\text{ONC})_2\text{KCN}$, or $\text{Hg}(\text{ONC})_2\text{KI}$, gives its 4-*CN*-derivative, m.p. 218—220°, which with 30% KOH or 66% H_2SO_4 yields the 4-carboxylamide, m.p. 223°. Similarly 3-methyl-5-pyrazolone yields the substance, $\text{C}_5\text{H}_5\text{ON}_3$, m.p. 281—283° (decomp.), and 1:3-diphenyl-5-pyrazolone gives its 4-cyano-derivative, m.p. 232—233°, hydrolysed (66% H_2SO_4) to the 4-carboxylamide, m.p. 227—228°.

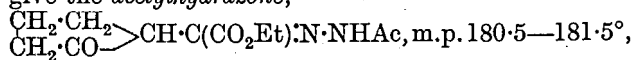
E. W. W.

Pyrazolones.—See B., 1938, 1271.

Trimethylene-pyrazoles and -hydroxypyridazones. K. von AUWERS and W. NOLL (Annalen, 1938, 536, 97—116).—In their chemical properties the trimethylenepyrazoles closely resemble the ring-homologous tetrahydroindazoles. *Et cyclopentanoneoxalate*, b.p. 135—140°/12 mm., m.p. 29.5—30.5°, obtained in 70% yield by addition of well-cooled NaOEt-EtOH to a well-cooled mixture of *cyclopentanone* and $\text{Et}_2\text{C}_2\text{O}_4$ (semicarbazone, m.p. 179—180°), is transformed by N_2H_4 at 0° or room temp. into *Et 2-amino-4:5-trimethylenepyrazole-3-carboxylate* (I), m.p. 165° (decomp.) when moderately rapidly heated, 4-hydroxy-5:6-trimethylenepyridaz-3-one (II), m.p. 254—256°, *Et 4:5-trimethylenepyrazole-3-carboxylate* (III), m.p. 125°, and a substance, $\text{C}_{18}\text{H}_{22}\text{O}_5\text{N}_2$, m.p. 166—166.5°. (I) passes when melted into (III), also obtained by treating (I) with HNO_2 . If the solution of (I) in Ac_2O is allowed to evaporate, *Et 2-acetamido-4:5-trimethylenepyrazole-3-carboxylate*, m.p. 63—64°, is obtained. With $p\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$ (I) gives the substance (IV), m.p. 299° (decomp.). 2-Amino-4:5-trimethylenepyrazole-3-carboxylic acid has m.p. 283°. (II) (*Na* and NH_4 salts; *Ac* derivative, m.p. 164—165°) could not be methyl-



ated with MeI in presence or absence of alkali. (III), which does not yield a picrate, is readily hydrolysed by KOH-EtOH to 4:5-trimethylenepyrazole-3-carboxylic acid, m.p. 282° after darkening at 250° according to rate of heating. The ester is transformed by EtI and NaOEt in boiling EtOH into a mixture of esters, hydrolysed to a mixture of acids, which are separated from one another by boiling HCl-MeOH , thus giving *Me 1-ethyl-4:5-trimethylenepyrazole-3-carboxylate*, b.p. 178—179°/12 mm. (corresponding acid, m.p. 180.5°), and 2-ethyl-4:5-trimethylenepyrazole-3-carboxylic acid, m.p. 178—179°. Boiling Ac_2O transforms (III) into the *Ac* derivative, m.p. 67.5°. *Et cyclopentanoneoxalate* and NHAcNH_2 give the *acetylhydrazone*,



which could not be satisfactorily cyclised by POCl_3 . The difficulty in obtaining a good yield of 1-hydroxymethylenecyclopentan-2-one from *cyclopentanone* and HCO_2Et is due in part to the production of 1:3-dihydroxymethylenecyclopentan-2-one, m.p. 115.5—116.5°. 4:5-Trimethylenepyrazole is therefore preferably obtained (65% yield) by decarboxylation of the 3-carboxylic acid by heating with Cu powder in N_2 ; it has m.p. 58° (*picrate*, m.p. 138.5°; hygroscopic *hydrochloride*, m.p. 203.5—204.5°). Treatment of it with NaOMe and MeI in boiling MeOH affords the *picrate*, m.p. 274°, of an unidentified substance, 1-methyl-4:5-methylenepyrazole (*picrate*, m.p. 173—174°), and 2-methyl-3:4-trimethylenepyrazole (*picrate*, m.p. 175.5—176°). According to conditions the condensation of *Et cyclopentanoneoxalate* with NHMeNH_2 gives varying proportions of 4-hydroxy-2-methyl-5:6-trimethylenepyridaz-3-one, m.p. 206—207° (*Ac* derivative, m.p. 83—84°), the *methylhydrazone* of *cyclopentanoneoxalic acid*, m.p. 248—248.5° after darkening at about 238°, transformed by short treatment with boiling Ac_2O into the *Ac* compound of the corresponding lactone, $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$, m.p. 193—194°, and a mixture of esters converted by NaOH into 2-methyl-4:5-trimethylenepyrazole-3-carboxylic acid, m.p. 200.5° (non-cryst. *Me* ester), and the 1-*Me* acid, m.p. 207—208° (decomp.) (*Me* ester, m.p. 96.5—97°). Similar condensation with NHPhNH_2 leads to 2-phenyl-4:5-trimethylenepyrazole-3-carboxylic acid, m.p. 217.5°, *Me 1-phenyl-4:5-trimethylenepyrazole-3-carboxylate*, m.p. 140.5° [corresponding acid, m.p. 216.5° (slight decomp.)], and 4-hydroxy-2-phenyl-5:6-trimethylenepyridaz-3-one, m.p. 217.5°. 1-Methylcyclopentan-3-one, $\text{Et}_2\text{C}_2\text{O}_4$, and NaOEt-EtOH at -5° afford *Et 1-methylcyclopentan-3-one-4-oxalate*, b.p. 141°/12 mm., transformed by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in EtOH at 0° and subsequently at room temp. into 4-hydroxy-5:6-2'-methyltrimethylenepyridaz-3-one, m.p. 225—225.5° (*Ac* derivative, m.p. 179°), and *Et 4:5-2'-methyltrimethylenepyrazole-3-carboxylate*, m.p. 120° [corresponding acid, m.p. 225—225.5° (decomp.)]. Analogously NHMeNH_2 yields 4-hydroxy-2-methyl-5:6-2'-methyltrimethylenepyridaz-3-one, m.p. 158—159°, *Me 1-methyl-4:5-2'-methyltrimethylenepyrazole-3-carboxylate*, b.p. 138—140°/12 mm. (corresponding acid, m.p. 175—175.5°), and non-homogeneous 2-methyl-4:5-2'-methyltrimethylenepyrazole-3-carboxylic acid.

H. W.

Pyrazoline local anaesthetics. II. Derivatives of alkylated 3 : 4-dihydroxybenzylideneacetones. H. B. NISBET. **III. Derivatives of *o*-alkoxybenzylideneacetones.** G. A. LEVY and H. B. NISBET (J.C.S., 1938, 1568—1571, 1572—1574).—II. *Ethyl*- and *ethyliso-vanillylideneacetone* have m.p. 105° and 92—93°, respectively. Condensation of these ketones and veratrylidene-, piperonylidene-, and vanillylidene-acetone with CH_2O and the hydrochlorides of NHMe_2 , NHEt_2 , or $\text{C}_5\text{H}_{11}\text{N}$ gives a series of unsaturated amino-ketones. Isomerisation (AcOH) of the phenyl- or *p*-tolyl-hydrazones affords the corresponding pyrazolines. The introduction of alkoxy groups into the 5-Ph nucleus increases the local anaesthetic activity and decreases the toxicity. The following are described: *phenylhydrazone*, m.p. 175°, of 1-diethylamino-5-(3' : 4'-dimethoxyphenyl)- Δ^4 -penten-3-one hydrochloride; 1-phenyl-5-(3' : 4'-dimethoxyphenyl)-3- β -diethylaminoethylpyrazoline, m.p. 93—96° (acid succinate, m.p. 94—95°); 1-phenyl-5-(3' : 4'-dimethoxyphenyl)-3- β -piperidinoethylpyrazoline, m.p. 79—84° (acid sulphate, m.p. 157—160°); 1-dimethylamino-5-(3' : 4'-methylenedioxyphenyl)- Δ^4 -penten-3-one hydrochloride, m.p. 163—164°; 1-phenyl-5-(3' : 4'-methylenedioxyphenyl)-3- β -dimethylaminoethylpyrazoline hydrochloride, m.p. 194°; 1-*p*-tolyl-5-(3' : 4'-methylenedioxyphenyl)-3- β -dimethylaminoethylpyrazoline hydrochloride, m.p. 182—184°; 1-phenyl-5-(3' : 4'-methylenedioxyphenyl)-3- β -piperidinoethylpyrazoline hydrochloride, m.p. 196—197°; 1-dimethylamino-5-(4'-methoxy-3'-ethoxyphenyl)- Δ^4 -penten-3-one hydrochloride, m.p. 161—162° [*phenylhydrazone*, m.p. 178°; *p*-tolylhydrazone (+1.5 H_2O), m.p. 173°]; 1-phenyl-5-(4'-methoxy-3'-ethoxyphenyl)-3- β -dimethylaminoethylpyrazoline hydrochloride (+ H_2O), m.p. 152°; 1-diethylamino-5-(4'-methoxy-3'-ethoxyphenyl)- Δ^4 -penten-3-one hydrochloride, m.p. 132—134° (*phenylhydrazone*, m.p. 173°); 1-phenyl-5-(4'-methoxy-3'-ethoxyphenyl)-3- β -diethylaminoethylpyrazoline, m.p. 50—51°; 1-piperidino-5-(4'-methoxy-3'-ethoxyphenyl)- Δ^4 -penten-3-one hydrochloride, m.p. 162° (*phenyl*-, m.p. 184°, and *p*-tolylhydrazone, m.p. 183°); 1-phenyl-, m.p. 192°, and 1-*p*-tolyl-5-(4'-methoxy-3'-ethoxyphenyl)-3- β -piperidinoethylpyrazoline hydrochloride (+ H_2O), m.p. 178°; 1-dimethylamino-5-(3'-methoxy-4'-ethoxyphenyl)- Δ^4 -penten-3-one hydrochloride, m.p. 165° (*phenyl*-, m.p. 177°, and *p*-tolylhydrazone, m.p. 174°); 1-phenyl-5-(4'-methoxy-3'-ethoxyphenyl)-3- β -dimethylaminoethylpyrazoline hydrochloride (+1.5 H_2O), m.p. 181°; 1-piperidino-5-(3'-methoxy-4'-ethoxyphenyl)- Δ^4 -penten-3-one hydrochloride, m.p. 167° (*phenyl*-, m.p. 167°, and *p*-tolylhydrazone, m.p. 176—178°); 1-phenyl-, m.p. 172—173°, and 1-*p*-tolyl-5-(3'-methoxy-4'-ethoxyphenyl)-3- β -piperidinoethylpyrazoline hydrochloride, m.p. 183°; 1-piperidino-5-*vanillyl*- Δ^4 -penten-3-one hydrochloride, m.p. 180° (*phenylhydrazone*, m.p. 196°); and 1-phenyl-5-*vanillyl*-3- β -piperidinoethylpyrazoline, m.p. 174°. (I) has been resolved through the acid tartrate, m.p. 134°, $[\alpha]_D^{25} -36.7^\circ$; this resolution has but little effect on the anaesthetic activity.

III. By alkylating salicylideneacetone and condensing the products with CH_2O and $\text{C}_5\text{H}_{11}\text{N}$, HCl , a series of unsaturated β -amino-ketones has been

obtained. The phenylhydrazones of these have been isomerised to pyrazolines; pharmacological examination indicates that, the *o*-*n*-OPr-compound excepted, they are better local anaesthetics than cocaine for rabbit's cornea and in the human wheal test. The following are described: 2-*ethoxy*-, b.p. 143—145°/1 mm., 2-*n-propoxy*-, b.p. 155—165°/1 mm., and 2-*n-butoxy-benzylideneacetone*, b.p. 177.5°/3 mm.; 1-piperidino-5-(2'-methoxyphenyl)- Δ^4 -penten-3-one hydrochloride, m.p. 177—178° (*phenylhydrazone*, m.p. 160—162°); 1-phenyl-5-(2'-methoxyphenyl)-3- β -piperidinoethylpyrazoline hydrochloride, m.p. 74—75°; 1-piperidino-5-(2'-ethoxyphenyl)- Δ^4 -penten-3-one hydrochloride, m.p. 190° (*phenylhydrazone*, m.p. 165—167°); 1-phenyl-5-(2'-ethoxyphenyl)-3- β -piperidinoethylpyrazoline hydrochloride, m.p. 166°; 1-piperidino-5-(2'-*n-propoxyphenyl*)- Δ^4 -penten-3-one hydrochloride, m.p. 182° (*phenylhydrazone*, m.p. 161—162°); 1-phenyl-5-(2'-*n-propoxyphenyl*)-3- β -piperidinoethylpyrazoline hydrochloride, m.p. 193.5°; 1-piperidino-5-(2'-*n-butoxyphenyl*)- Δ^4 -penten-3-one hydrochloride, m.p. 164—165° (*phenylhydrazone*, m.p. 154—155°); 1-phenyl-5-(2'-*n-butoxyphenyl*)-3- β -piperidinoethylpyrazoline hydrochloride, m.p. 191°; and 1-diethylamino-5-(2'-*n-butoxyphenyl*)- Δ^4 -penten-3-one hydrochloride, m.p. 115—116° (*phenylhydrazone*, m.p. 141°). F. R. S.

Physiological importance in nutrition of methods of preparation of foodstuffs. IV. Coupling of histidine and histamine with diazonium salts. W. DIEMER and H. FOX (Biochem. Z., 1938, 298, 38—50; cf. A., 1937, III, 466).—Chromatographic adsorption analysis (Al_2O_3 as adsorbent) of the coloured substances produced shows that, usually, there are several reaction products. When Na *p*-nitrophenylantidiazotate is used there are only two products if the p_{H} of the medium is kept const. after making slightly alkaline with NaHCO_3 .

W. McC.

New group of crystalline-liquid substances, the homologous *pp'*-diphenylpyridazines. C. WEYGAND and W. LANZENDORF (J. pr. Chem., 1938, [ii], 151, 221—226).—Cryst.-liquid phases are observed with all disubstituted *pp'*-diphenylpyridazines but not with the corresponding singly substituted compounds. The following *-diphenylpyridazines* are described: *pp'*-dimethyl-, m.p. 233°; *pp'*-diethyl-, m.p. 206°; *pp'*-dipropyl-, m.p. 204°; *pp'*-dibutyl-, m.p. 207°; *pp'*-diamyl-, m.p. 194°; *pp'*-dihexyl-, m.p. 187°; *p*-methyl-, m.p. 188°; *p*-ethyl-, m.p. 176°; *p*-propyl-, m.p. 155°; *p*-butyl-, m.p. 158°; *p*-amyl-, m.p. 164°. H. W.

Action of substituted hydrazines on 1 : 4-diketones. I, II. S. CAPUANO (Gazzetta, 1938, 68, 521—527, 527—532).—I. $\text{NHBz}\cdot\text{NH}_2$ and $\text{CHPhBz}\cdot\text{CH}_2\text{Bz}$ (I) in boiling AcOH give, with a *N*-free substance, m.p. 51°, 1-benzoyl-3 : 4 : 6-triphenyl-1 : 2-dihydropyrazine, m.p. 265—266° (or 256°?) (*p*-nitrophenylhydrazone, m.p. 233—234°), which, stable to boiling 30% KOH - EtOH and to 5—30% HCl or H_2SO_4 , is oxidised by CrO_3 - AcOH to triphenylpyridazine and BzOH .

II. With $\text{CHPh}\cdot\text{N}\cdot\text{NH}_2$ in boiling AcOH , (I) gives 1 : 2-dihydro-3 : 4 : 6-triphenylpyridazine, m.p. 187°,

3 : 4 : 6-triphenylpyridazine, m.p. 172—173°, and *desylacetophenonetrihydrazone*, m.p. 100° (which with 20% HCl in EtOH gives a *polymeride*, m.p. 147°, of *desylacetophenone*). E. W. W.

Derivatives of $\alpha\gamma$ -dianilinopropane. W. L. C. VEER (Rec. trav. chim., 1938, 57, 987—1015).— $\text{CH}_2(\text{CH}_2\text{NHPH}_2)$ (I), m.p. 40—41°, b.p. 244—245°/11 mm., 251—253°/19 mm. (lit., b.p. 280—285°/16 mm.), yields a *dinitrate*, m.p. 155—160° (decomp.), and Ac_2 , (II), m.p. 119° (by $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ or $\text{CH}_2\text{:CO}$ in Et_2O), Bz_2 , m.p. 135°, and NN' -*biscarbomethoxy*-, m.p. 69°, -derivatives. With MeNCO , PhNCO , MeNCS , and PhNCS , (I) yields respectively the $\alpha\gamma$ -*bis-methylcarbamyl*, m.p. 153—155°, -*phenylcarbamyl*, m.p. 154—157°, -*methylthiocarbamyl*, m.p. 202° (block), and -*phenylthiocarbamyl*, m.p. 151°, derivatives. With C_3O_2 , 6 : 8-diketo-1 : 5-diphenyl-1 : 5-diazocyclooctane, m.p. 117° (indef.), is formed. With PhCHO , $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$, $p\text{-NO}_2\text{-C}_6\text{H}_4\cdot\text{CHO}$, and *furfuraldehyde* (I) yields respectively 2-phenyl-, m.p. 120°, 2-*chlorophenyl*-, 2-*p-nitrophenyl*-, and 2- α -furyl-1 : 3-diphenylhexahydropyrimidine, m.p. 138.5°. No reaction occurs with MeCHO , EtCHO , *o*- or *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, or 5-methylfurfuraldehyde. Repeated nitration of (I) with pure HNO_3 below 0° yields $\alpha\gamma$ -di-[(2 : 4 : 6-trinitrophenyl)nitroamino]propane (III), m.p. 189°.

$\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ and $\text{NH}_2\cdot[\text{CH}_2]_3\cdot\text{NH}_2$ (IV) {which could not be produced from $\text{Br}\cdot[\text{CH}_2]_3\cdot\text{Br}$ (V) and aq. NH_3 } yield $\alpha\gamma$ -di-(2-nitroanilino)propane, converted by nitration into (III). $p\text{-NO}_2\text{-C}_6\text{H}_4\cdot\text{NH}_2$ and (V) at 150°, or $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ and (IV), yield $\alpha\gamma$ -di-(4-nitroanilino)propane [Ac derivative (VI), m.p. 170°], also converted by nitration into (III). Similarly (IV) with 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ and picryl chloride yields respectively $\alpha\gamma$ -di-(2 : 4-dinitroanilino)-, m.p. 233° [Ac derivative, m.p. 121° (indef.)], and $\alpha\gamma$ -di-(2 : 4 : 6-trinitroanilino)-propane, m.p. 199° [Ac derivative (+ $\frac{1}{2}$ mol. dioxan), m.p. 151°], both of which are converted by nitration into (III). Hydrolysis of (III) (Na_2CO_3) yields picric acid. Nitration of (II) yields (VI). $\alpha\gamma$ -Di-(*p*-tolylamino)propane (VII) (Ac_2 derivative, m.p. 120°; *bis-phenylthiocarbamyl* derivative, m.p. 152—154°) with CH_2O yields 1 : 3-di-*p*-tolylhexahydropyrimidine, and with $p\text{-NO}_2\text{-C}_6\text{H}_4\cdot\text{CHO}$ 1 : 3-di-*p*-tolyl-2-*p*-nitrophenylhexahydropyrimidine, m.p. 155°. Repeated nitration of (VII) (pure HNO_3) yields $\alpha\gamma$ -di-(2 : 6-dinitro-4-tolyl)nitroamino]propane, (VIII), m.p. 173°, the structure of which is proved as follows.

2 : 6-Dinitro-4-methylanisole (IX) and (IV) in EtOH yield $\alpha\gamma$ -di-(2 : 6-dinitro-4-tolylamino)propane, m.p. 206° (Ac_2 derivative, m.p. 184°), which when nitrated yields (VIII). Similarly, (IX) and $(\text{CH}_2\text{NH}_2)_2$ yield $\alpha\beta$ -di-(2 : 6-dinitro-4-tolylamino)ethane, m.p. 233°, nitrated to $\alpha\beta$ -di-[(2 : 6-dinitro-4-tolyl)nitroamino]ethane. $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, NaOAc , and (V) yield $\alpha\gamma$ -di-(*p*-chloranilino)propane, m.p. 75° (Ac_2 derivative, m.p. 128°), nitrated to $\alpha\gamma$ -di-[(4-chloro-2 : 6-dinitrophenyl)nitroamino]propane, m.p. 159°, also formed by nitration of $\alpha\gamma$ -di-(4-chloro-2 : 6-dinitroanilino)propane, m.p. 217° (Ac_2 derivative, m.p. 204°) [(formed from 4 : 2 : 6 : 1- $\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2\cdot\text{OMe}$ and (IV)]. Similarly from *p*-

$\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ is formed $\alpha\gamma$ -di-(*p*-bromoanilino)propane, m.p. 96° (Ac_2 derivative, m.p. 134°), nitrated to $\alpha\gamma$ -di-[(4-bromo-2 : 6-dinitrophenyl)nitroamino]propane, m.p. 167°, also formed by nitration of $\alpha\gamma$ -di-(4-bromo-2 : 6-dinitroanilino)propane, m.p. 194° (Ac_2 derivative, m.p. 190°) [from 4 : 2 : 6 : 1- $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\cdot\text{OMe}$ and (IV)]. 3 : 4-Dinitro-chloro- or -bromo-benzene with (IV) yields respectively $\alpha\gamma$ -di-(5-chloro-, m.p. 205° (indef.), and -5-bromo-2-nitroanilino)propane, m.p. 226° (Ac_2 derivative, m.p. 137°), which are nitrated to $\alpha\gamma$ -[di-(5-chloro-, m.p. about 100°, and -(5-bromo-2 : 4 : 6-trinitrophenyl)nitroamino]propane, m.p. 117°, respectively. 1 : 3 : 4 : 5- $\text{C}_6\text{H}_3\text{Cl}_2(\text{NO}_2)_2$ or - $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)_2$ with $(\text{CH}_2\text{NH}_2)_2$ yields $\alpha\beta$ -di-(4 : 6-dichloro-, m.p. 135° (Ac_2 derivative, m.p. 242°; *dinitroamine*, m.p. 196°), or -dibromo-2-nitroanilino)ethane, m.p. 134° (Ac_2 derivative, m.p. 251°; *dinitroamine*, m.p. 207°). Similarly from (IV) are formed $\alpha\gamma$ -di-(4 : 6-dichloro-, m.p. 124° (Ac_2 derivative, m.p. 163°; *dinitroamine*, m.p. 149°), and -dibromo-2-nitroanilino)propane, m.p. 138° (Ac_2 derivative, m.p. 155°; *dinitroamine*, m.p. 199°). J. D. R.

Catalytic reduction of organic halogen compounds : 5-chloro-5-alkylbarbituric acids. G. K. HUGHES and A. K. MACBETH (J.C.S., 1938, 1622—1624).—5-Chloro-5-methyl-, m.p. 201—202°, -ethyl-, m.p. 191—192°, -*n*-propyl-, m.p. 190—191°, -isopropyl-, m.p. 188—189°, -*n*-butyl-, m.p. 138—139°, and -isoamyl-barbituric acid, m.p. 164—165°, are rapidly reduced in EtOH- H_2O in the presence of colloidal Pt; the unimol. reaction rate is determined conductometrically. In general, the velocity coeff. varies but little with the alkyl group, the Pr^i acid being exceptional. The reduction of the Cl-acids is quicker than that of the corresponding Br-derivatives, the ratio in the cases examined being about 4. The Cl in the Cl-acids is also removed by N_2H_4 . F. R. S.

Colour in relation to chemical constitution of organic and inorganic salts of oximinodiphenylthiobarbituric acid and its higher homologues and analogues. I. N. D. DASS and S. DUTT (Proc. Indian Acad. Sci., 1938, 8, A, 145—159).— $\text{CS}(\text{NHPh})_2$ and $\text{CH}_2(\text{CO}_2\text{H})_2$ in boiling AcCl give *diphenylthiobarbituric acid*, m.p. 245°, converted by NaNO_2 in 5% aq. NaOH into *oximinodiphenylthiobarbituric acid* (*diphenylthiovioluric acid*) (I), m.p. 227° and 220° (two forms). The following thiobarbituric acids are prepared as above : *di-o*-, m.p. 190°, -*m*-, m.p. 265°, and -*p*-tolyl-, m.p. 233°; *di-m*-xylyl-, m.p. 247°, -*o*-anisyl-, m.p. 248°, -*p*-phenetyl-, m.p. 167°, and -1-naphthyl-thiobarbituric acid, m.p. 216°. The above thiobarbituric acids are converted, respectively, by NaNO_2 into the following thiovioluric acids : *di-o*-, m.p. 200°, -*m*-, m.p. 216°, and -*p*-tolyl-, m.p. 128°, -*m*-xylyl-, m.p. 165°, -*o*-anisyl-, m.p. 212°, -*p*-phenetyl-, m.p. 128°, and -1-naphthyl-thiovioluric acid, m.p. 216°. (I) may exist in the oximino-ketonic or the nitroso-enolic form. The latter is the more acidic and represents the structure of the highly coloured thioviolurates. The colour is explained on Dutt's hypothesis (A., 1926, 830; 1927, 1006) as being due to the highly strained $\cdot\text{N}:\text{O}$ chromo-

phore. (I) with org. bases in dry COME_2 gives yellow or orange additive products, but in presence of a little H_2O , intensely coloured salts are formed. Very weak bases like $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ and *m*-xylydine do not form salts with (I). The following -thioviolurates are described: NH_2Me , m.p. 128° , NHMe_3 , m.p. 185° , NMe_3 , m.p. 123° , NH_2Et , m.p. 176° , NHEt_2 , m.p. 128° , *allylamine*, m.p. 169° , $\text{NH}_2\text{Bu}^\beta$, m.p. 178° , *isoamylamine*, m.p. 162° , *quinoline*, m.p. 176° , *isoquinoline*, m.p. 174° , *piperidine*, m.p. 184° , *collidine*, m.p. 186° , $\text{C}_5\text{H}_5\text{N}$, m.p. 178° , α -*picoline*, m.p. 188° , *lepidine*, m.p. 186° , *quinaldine*, m.p. 159° , *phenetidine*, m.p. 136° , *anisidine*, m.p. 128° , $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, m.p. 161° , *o*-, m.p. 180° , *m*-, m.p. 164° , and $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, m.p. 199° , *brucine*, m.p. 180° , *K*, m.p. 219° , *Na*, m.p. 128° , NH_4 , m.p. 213° , *quinine*, m.p. 139° , *veratrine*, m.p. 168° , *cinchonidine*, m.p. 140° , *morphine*, m.p. 93° , *thebaine*, m.p. 123° , and *narcotine* *diphenylthioviolurate*, m.p. 103° . NH_2Me , m.p. 153° , NHEt_2 , m.p. 181° , NEt_3 , m.p. 155° , *quinoline*, m.p. 212° , and *Na di-o-tolylthioviolurate*. NH_2Me , m.p. 176° , NHEt_2 , m.p. 142° , NMe_3 , m.p. 164° , and *Na di-p-tolylthioviolurate*. NH_2Me , m.p. 160° , NHEt_2 , m.p. 185° , NMe_3 , m.p. 107° , *quinoline*, m.p. 177° , and *Na di-m-tolylthioviolurate*. NH_2Me , m.p. 148° , NHEt_2 , m.p. 104° , NMe_3 , m.p. 138° , and *Na di-m-xylylthioviolurate*. NH_2Me , m.p. 151° , NHEt_2 , m.p. 154° , NMe_3 , m.p. 105° , and *Na di-o-anisylthioviolurate*. NH_2Me , m.p. 142° , NHEt_2 , m.p. 136° , NMe_3 , m.p. 114° , *Na*, and *quinoline di-p-phenetylthioviolurate*, m.p. 136° . NH_2Me , m.p. 147° , NHEt_2 , m.p. 153° , NMe_3 , m.p. 112° , and *Na di- α -naphthylthioviolurate*. The colours of the above salts range from bluish-green to deep emerald-green with absorption max. usually at about 6500 Å. The intensity of the colour is approx. cc the strength of the base. *m*-Substituted Ph derivatives have a somewhat more intense colour than those with *p*-substituents. The effect of S in changing the colour (pink) of violurates (II) to that (violet) of thioviolurates is about the same as that of 2Ph in changing the colour of (II) to that (violet) of diphenylviolurates. The effect of substituents on the colour of the compounds is explained in the light of Dutt's theory (*loc. cit.*). Tables are compiled showing the absorption max. of many (II), thioviolurates, and diphenylthioviolurates.

J. L. D.

Iminazoles. II. Synthesis of tetrahydrobenziminazole (4:5-cyclotetramethyleneglyoxaline) and its derivatives. R. WEIDENHAGEN and H. WEGNER (*Ber.*, 1938, 71, [B], 2124—2134; cf. A., 1938, II, 30).—Benziminazole is not hydrogenated (Ni-Mo on SiO_2) at about $180^\circ/90$ atm. *cyclohexanolone* (I) (modified prep.) is converted by $\text{Cu}(\text{OAc})_2$, CH_3O , NH_3 , and NaOH in $\text{EtOH-H}_2\text{O}$ and treatment of the product with H_2S into *tetrahydrobenziminazole* (II), m.p. $149\text{--}150^\circ$ (Cu derivative; *picrate*, m.p. $189\text{--}190^\circ$ after slight softening). When gradually treated with BzCl in $\text{C}_5\text{H}_5\text{N}$ at 0° it gives 1-benzoyltetrahydrobenziminazole, m.p. $131\text{--}132^\circ$. It is converted by BzCl and NaOH at 0° into 1:2-dibenzamido- Δ^1 -cyclohexene, m.p. $266\text{--}267^\circ$, which does not couple and is insol. in NaHCO_3 or Na_2CO_3 . Attempted dehydrogenation (Pd sponge) of (II) leads to a compound, $(\text{C}_7\text{H}_8\text{ or }9\text{N}_2)_x$, m.p. $>300^\circ$.

Oxidation of (II) by KMnO_4 causes complete disruption of the mol.; the formation of adipic acid or of glyoxaline-4:5-dicarboxylic acid could not be detected. Similarly by use of the requisite aldehyde the following -tetrahydrobenziminazoles are obtained: 2-methyl-, m.p. $221\text{--}222^\circ$ (Cu compound; *picrate*, m.p. $185\text{--}186^\circ$); 2-ethyl-, m.p. $196\text{--}197^\circ$ (Cu compound; *picrate*, m.p. $145\text{--}146^\circ$); 2-n-propyl-, m.p. $185\text{--}186^\circ$ (Cu compound; *picrate*, m.p. $115\text{--}116^\circ$); 2-isopropyl-, m.p. $240\text{--}241^\circ$ [Cu compound; *picrate*, m.p. (indef.), $90\text{--}93^\circ$]; 2-isobutyl-, m.p. 206° (Cu derivative), does not give a cryst. *picrate*; 2-hexyl-, m.p. $157\text{--}158^\circ$ (Cu salt; *picrate*, m.p. $142\text{--}144^\circ$); 2-phenyl-, m.p. $290\text{--}291^\circ$ after softening at 285° [Cu derivative; *hydrochloride*, m.p. $249\text{--}251^\circ$; *picrate*, m.p. 258° (decomp.)]; 2-furyl-, decomp. $290\text{--}300^\circ$ after softening $>200^\circ$ [Cu salt; *hydrochloride*; *picrate*, m.p. $220\text{--}225^\circ$ (decomp.)]; 2-anisyl-, m.p. $236\text{--}238^\circ$ (Cu salt; *hydrochloride*; *picrate*, m.p. $211\text{--}212^\circ$). 4-Methylcyclohexanolone and the requisite aldehyde give the following -tetrahydrobenziminazoles; 5-methyl-, b.p. $138^\circ/0.4$ mm., m.p. $117\text{--}118^\circ$ (Cu salt); 2:5-dimethyl-, m.p. 184° (Cu derivative); 5-methyl-2-ethyl-, m.p. $204\text{--}205^\circ$ (Cu salt); 5-methyl-2-n-propyl-, m.p. $183\text{--}184^\circ$ (Cu salt). H. W.

Benziminazoles.—See B., 1938, 1270.

Polypyridyls. F. H. BURSTALL (*J.C.S.*, 1938, 1662—1672).—2-Bromopyridine (I) and Cu in Ph_2 give 2:2'-dipyridyl (II), which is brominated at 500° to 6-bromo-, m.p. 74° , and 6:6'-dibromo-2:2'-dipyridyl, m.p. 218° . Bromination of 2:2'-dipyridyl hydrobromide at 250° yields 5(?)-bromo-, m.p. 79° , and 5:5' (?) -dibromo-2:2'-dipyridyl, m.p. $212\text{--}213^\circ$. Treatment of the 6-compounds with the appropriate reagent leads to 6-amino-, m.p. 89° , 6:6'-diamino-, m.p. 185° , 6-cyano-, m.p. 151° , and 6:6'-dicyano-2:2'-dipyridyl, m.p. 255° , and 2:2'-dipyridyl-6-carboxylic acid, m.p. $210\text{--}220^\circ$, and 6:6'-dicarboxylic acid, m.p. 286° . 6-Bromo-2:2'-dipyridyl and (I) with Cu afford a mixture of (II), 6:6'-di-2''-pyridyl-2:2'-dipyridyl [2:2':2'':2'''-tetrapyridyl] (III), m.p. $219\text{--}220^\circ$ [*hydrochloride* (+ $3\text{H}_2\text{O}$); *dipicrate*, m.p. 312° (decomp.)], and 2:6-di-2'-pyridylpyridine. The latter compound is brominated to 6'-bromo-, m.p. 153° , and 6':6''-dibromo-2:6-di-2'-pyridylpyridine (IV), m.p. 248° . (II) and I at 310° give a mixture of (III) and 6:6'-di-2''-pyridyl-2:3'-dipyridyl, m.p. 141° ; (III) is also obtained by the action of Cu on a mixture of (I) and 2:6-dibromopyridine. 4:4'-Dipyridyl and I afford 4:4'-di-4''-pyridyl-2:2'-dipyridyl, m.p. $232\text{--}233^\circ$, and the 3:4'-compound yields 4:4'-di-3''-pyridyl-2:2'-dipyridyl, m.p. 222° . 5(?) -Bromo-2:2'-dipyridyl and Cu form 6:6'-di-2''-pyridyl-3:3'-dipyridyl, m.p. 233° . Cu with (I) and (IV) gives 2:6-di-6''-(2':2''-dipyridyl)pyridine [2:2':2'':2'''-pentapyridyl], m.p. 265° [*hydrochloride* (+ $2\text{H}_2\text{O}$)], also obtained from Cu, 6-bromo-2:2'-dipyridyl, and 2:6-dibromopyridine. 2:6-Di-2'-pyridylpyridine and I afford 6:6'-di-6''-(2':2''-dipyridyl)-2:2'-dipyridyl [2:2':2'':2'''-2''':2''''-hexapyridyl], m.p. 350° (tetrahydrochloride), also obtained by the action of Cu on the appropriate Br-compounds. F. R. S.

Reaction of azobenzene with some pyrazolone derivatives. M. PASSERINI and G. LOSCO (Gazzetta, 1938, 68, 485—488).—Benzylidenebis-1-phenyl-3-methyl-5-pyrazolone and $(NPh)_2$ (I) at 180° give $CHPh:NPh$ and *bis*-(5-keto-1-phenyl-3-methyl-4-pyrazolyl), m.p. $>320^\circ$. This is also obtained, with the appropriate anils, when the salicylidene or anisylidene derivatives are used, or (I) and 1-phenyl-3-methyl-5-pyrazolone itself $[(NHP)_2]$ or NH_2Ph not isolated]. E. W. W.

2-Methylindole and 1-phenyl-3-methyl-5-pyrazolone. M. PASSERINI (Gazzetta, 1938, 68, 480—484).—2-Methylindole (I) and HCO_2H give, in addition to 2-methyl-3-indolyl-2'-methyl-3'-indolidenemethane (II) (A., 1913, i, 895), *tris*-(2-methyl-3-indolyl)methane (III), m.p. 319° . Similarly (II) with cold HCO_2H or $AcOH$ and (I) gives (III). Under similar conditions (II) does not react with 1-phenyl-3-methyl-5-pyrazolone (IV), but when they are heated in $EtOH$ they give 5-keto-1-phenyl-3-methyl-4-pyrazolyl-5'-keto-1'-phenyl-3'-methyl-4'-pyrazolidenemethane, m.p. 181° , also formed, with (I), from (IV) and 2-methylindole-3-aldehyde. With $NPh:CH:NPh$, (IV) yields the *anil*, m.p. 153 — 155° , of its 4-aldehyde, and NH_2Ph .

E. W. W.

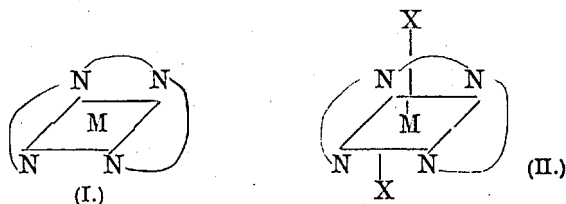
Nucleic acids. J. M. GULLAND (J.C.S., 1938, 1722—1734).—A lecture.

F. R. S.

Synthesis of 2:2'-diquinoxaliny. K. MAURER and B. BOETTGER (Ber., 1938, 71, [B], 2092—2094).—1:2-Dihydroquinoxalinyglycolaldehyde (A., 1938, II, 380) and $o-C_6H_4(NH_2)_2$ in boiling $MeOH$ containing $AcOH$ afford 2:2'-diquinoxaliny, m.p. 274° , also obtained by boiling quinoxaline-2-carboxylic acid with NH_2Ph . With conc. acids it separates salts which are immediately decomposed by H_2O . It is therefore not suited to complex formation. It is very resistant towards substitution. It could not be nitrated but is oxidised by strong nitrating acid. With 80% oleum it gives a *sulphonic acid*, m.p. 298 — 300° (Ba salt), in very modest yield. It does not react with cold alkyl halide but with MeI at 140° affords a *dimethiodide* (I), which loses MeI when heated and consequently has (apparent) m.p. 274° (corresponding *picrate*, m.p. 194° , and *perchlorate*). With $2N-NaOH$ (I) gives the corresponding yellow, free base which rapidly passes into the bright red *anhydride*, $C_{18}H_{16}ON_4$, m.p. 200° after softening at 160° . This with $EtOH$, $BaOH$, and $(CH_2OH)_2$ gives compounds, $C_{22}H_{16}O_2N_4$, $C_{26}H_{36}O_2N_4$, and $C_{26}H_{34}O_4N_4$, m.p. 162° , respectively. H. W.

Residual affinity and co-ordination. XXXVIII. Complex metallic salts containing 6:6'-di-2'-pyridyl-2:2'-dipyridyl (2:2':2'':2'''-tetrapyridyl). XXXIX. Complex ruthenium derivatives containing nitric oxide and polypyridyls. (Sir) G. T. MORGAN and F. H. BURSTALL (J.C.S., 1938, 1672—1675, 1675—1678).—XXXVIII. 6:6'-Di-2'-pyridyl-2:2'-dipyridyl combines with many metallic salts, forming co-ordination compounds of the types $[M \text{ tetpy}]X$, $[M \text{ tetpy}]X_2$, and $[MX_2 \text{ tetpy}]X$. With compounds of the two former types a planar arrangement (I), and with the latter type an octa-

hedral distribution (II), is probable; only one isomeride is obtained in each case.



The following salts have been obtained:

2:2':2'':2'''-tetrapyridyl-argentous nitrate, -ferrous sulphate tetrahydrate (anhyd. sulphate), -ferrous bromide dihydrate, -ferrous iodide trihydrate, -cobaltous chloride dihydrate and monohydrate, -cobaltic chloride trihydrate, -nickel bromide dihydrate, -cupric bromide hemihydrate, -zinc chloride dihydrate, -cadmium chloride hydrate, -dichloroiridium iridochloride, and platinous platinochloride, and 2:2':2'':2'''-tetrapyridyl platinochloride.

XXXIX. The nitrosoruthenium penta-chloride, -bromide, or -iodide with 2:2'-dipyridyl gives according to the conditions *trichloro-*, *tribromo-*, and *tri-iodo-nitroso-2:2'-dipyridylruthenium*, $[ONRuX_3dipy]$, and *chloronitrosobis-2:2'-dipyridyl-ruthenium nitrosoruthenium pentachloride*, $[ONRuCl_2dipy][ONRuCl_5]$; in acid solution, *bis-2:2'-dipyridylnitrosoruthenium pentachloride* ($+H_2O$) is obtained. In aq. medium 2:2':2'':2'''-tripyridyl affords *dichloronitroso-2:2':2''-tripyridylruthenium nitrosoruthenium pentachloride*, $[ONRuCl_2tripy]_2[ONRuCl_5]$, and *dichloronitroso-2:2':2''-tripyridylruthenium chloride* ($+3.5H_2O$); in acid solution, *2:2':2''-tripyridylnitrosoruthenium pentachloride* ($+H_2O$) is obtained. 2:2':2'':2'''-Tetrapyridyl similarly yields *chloronitroso-2:2':2'':2'''-tetrapyridylruthenium chloride pentahydrate*, *nitrosoruthenium pentachloride*, and *2:2':2'':2'''-tetrapyridylnitrosoruthenium pentachloride*. F. R. S.

Phthalocyanines.—See B., 1938, 1274.

Bile pigments. XX. Tetramethyl ester of *isohydroxycoproporphyrin* I. H. LIBOWITZKY and H. FISCHER (Z. physiol. Chem., 1938, 255, 209—233; cf. A., 1938, II, 160).—Coprohaemin ester I (I), treated with yeast in $C_5H_5N-H_2O$ through which air is passed and subsequently esterified with $MeOH + HCl$, gives a 9.96% yield of coproglaucobilin ester $I\alpha$ (II), the process being exactly analogous to reduction with ascorbic acid. The *pyridine-haemochromogen* (III), $C_{40}H_{44}O_8N_4Fe, 2C_5H_5N$, m.p. 158 — 162° (decomp.), corresponding with (II) is obtained in 91% yield from (I) in C_5H_5N by reduction in N_2 with $N_2H_4.H_2O$. (III) in C_5H_5N with Bz_2O_2 , followed by treatment with $AcOH$, $Fe(OAc)_2$, and HCl , gives coproporphyrin ester I. The same result is attained by treatment with aq. $KMnO_4$ or with CPh_3 in C_6H_6 in place of Bz_2O_2 ; in all cases Fe^{II} is converted into Fe^{III} . With H_2O_2 at 55° (III) in C_5H_5N is converted, in N_2 , into *isohydroxycoprohaemin ester* I (IV), $C_{40}H_{44}O_{10}N_4FeCl$, m.p. 260 — 265° (decomp.), which, when recryst. from $CHCl_3$ and $MeOH$ containing 1% of HCl , gives a reddish-brown pigment, m.p. 255 — 259° . (IV) in C_5H_5N gives with $BzCl$ followed by $Fe(OAc)_2$ a 52.5% yield of the α -benzoate (V), m.p. 242° , of copropor-

phyrin ester I and with Ac_2O in place of BzCl the corresponding α -acetate (VI), m.p. 199° , in 29% yield. (IV) with H_2O_2 followed by $\text{Fe}(\text{OAc})_2$ gives a 24% yield of the Me_4 ester I (VII), m.p. 258° , of *iso*-hydroxycoprotophyrin which with BzCl and Ac_2O gives (V) and (VI) respectively. (VII) reacts with PhNCO and $\alpha\text{-C}_{10}\text{H}_7\text{-NCO}$ and is reduced by Zn dust and by Na-Hg. Sunlight and electric light convert it into a violet-red compound. The hæmin of (VII) in $\text{C}_5\text{H}_5\text{N}$ is slowly converted by O_2 into a verdohæmatin which yields (II) when boiled with HCl in MeOH .

W. McC.

Benzoporphin. IV. Formation of tetrabenzoporphin from isoindole derivatives. J. H. HELBERGER and D. B. HEVER (Annalen, 1938, 536, 173—182; cf. A., 1938, II, 161).—Tetrabenzoporphin (I) and CuBr in boiling quinoline give the complex salt, $\text{C}_{36}\text{H}_{20}\text{N}_4\text{Cu}$. Carboxymethylenephthalimidine (II), which does not react with Cu salts, is converted by Mg , $\text{Mg}(\text{OAc})_2$, or $\text{Zn}(\text{OAc})_2$ at about 300° into the corresponding complex compounds of (I). Since much CO_2 is thereby evolved, the intermediate formation of methylenephthalimidine must be assumed. To obviate this (II) is converted by CH_3N_2 or MeOH-HCl into the *Me* ester, m.p. 123° , which, though sufficiently stable to be sublimed, is transformed by $\text{Zn}(\text{OAc})_2$ into the Zn complex of (I). This or the corresponding Mg compound is obtained from 3-ethylidenephthalimidine or 3-ethylphthalimidine, m.p. 105° (obtained by reduction in presence of Raney Ni), and $\text{Zn}(\text{OAc})_2$ or $\text{Mg}(\text{OAc})_2$ probably owing to elimination of *Me* from the CH bridge at the high temp. of the reaction. The action of $\text{Zn}(\text{OAc})_2$ at 200° on *N*-acetyl-3-methylphthalimidine or *N*-nitroso-3-methylphthalimidine, m.p. 87° , gives the same fugitive pigment as is obtained with 3-methylphthalimidine (III), which is the sole isolable product of the change. Dibromomethylphthalimidine, m.p. 236° , does not yield a dye. Phthalimidine and $\text{Zn}(\text{OAc})_2$ gives small amounts of the Zn complex of (I); AcOH from $\text{Zn}(\text{OAc})_2$ furnishes the methine bridge since no reaction is caused by use of ZnO , which is active in the case of (III). Phthalimide and $\text{Zn}(\text{OAc})_2$ at about 300° yield a mixture of the Zn salts of (I) and of tetrabenzomonoazaporphin, which cannot be separated chromatographically from one another, whereas with $\text{Fe}(\text{OAc})_2$ it gives homogeneous Fe^{II} tetrabenzoporphin. *N*-Methylphthalimide does not give dyes with acetates.

H. W.

Chemiluminescence of the chlorophylls and other porphyrin metal complex salts.—See A., 1938, I, 495.

Phenanthrene series. XXI. Morpholino-alcohols derived from phenanthrene. E. MOSERTIG, F. W. SHAVER, and A. BURGER (J. Amer. Chem. Soc., 1938, 60, 2464—2467).—The appropriate bromoacetylphenanthrene with morpholine in C_6H_6 gives 2-, m.p. $154\text{—}156^\circ$ [hydrochloride, m.p. 268° (decomp.)], and 3-morpholinoacetylphenanthrene, m.p. $136.5\text{—}137.5^\circ$ [hydrochloride, m.p. 237° (decomp.)], and 3-methoxy-9-morpholinoacetylphenanthrene hydrochloride, m.p. $240\text{—}242^\circ$ (decomp.). 2- and 3-Acetylphenanthrene, $(\text{CH}_2\text{O})_3$, and morpholine hydrochloride

in *iso*- $\text{C}_5\text{H}_9\text{-OH}$ give 2-, m.p. $120\text{—}130^\circ$ [hydrochloride, m.p. $224\text{—}226^\circ$ (decomp.)], and 3- β -morpholinopropionylphenanthrene, m.p. $114\text{—}116^\circ$ [hydrochloride, m.p. $207\text{—}208^\circ$ (decomp.)]. Similar reactions with bromoketo-1:2:3:4-tetrahydrophenanthrenes give 2-morpholino-1-keto-, m.p. $141\text{—}171^\circ$ (decomp.) [hydrochloride, m.p. $230\text{—}231^\circ$ (decomp.)], 3-morpholino-4-keto-, m.p. $127\text{—}128^\circ$ [hydrochloride, m.p. $227\text{—}228^\circ$ (decomp.)], 1-keto-2-morpholinomethyl-, m.p. 121° [hydrochloride, m.p. $182\text{—}183^\circ$ (decomp.)], and 4-keto-3-morpholinomethyl- [hydrochloride, m.p. $170\text{—}172^\circ$ (decomp.)]-1:2:3:4-tetrahydrophenanthrene. Hydrogenation (PtO_2) of the ketonic products gives 2-, m.p. $129\text{—}131^\circ$ [hydrochloride, m.p. $244\text{—}245^\circ$ (decomp.)], and 3- β -morpholino- α -hydroxyethyl-, m.p. $115\text{—}117^\circ$ [hydrochloride, m.p. 214° (decomp.)], 2-, m.p. $98\text{—}100^\circ$ [hydrochloride, m.p. $177\text{—}179^\circ$ (decomp.)]; *Ac* derivative hydrochloride, m.p. 253° (decomp.), and 3- γ -morpholino- α -hydroxy-*n*-propyl-phenanthrene, m.p. $83\text{—}86^\circ$ [hydrochloride, m.p. $172\text{—}174^\circ$ (decomp.)]; *Ac* derivative hydrochloride, m.p. $226\text{—}227^\circ$ (decomp.), 3-methoxy-9- β -morpholino- α -hydroxypropylphenanthrene hydrochloride, m.p. $217\text{—}219^\circ$ (decomp.), 1-hydroxy-2-morpholinomethyl-, m.p. $120\text{—}121^\circ$ [hydrochloride, m.p. $230\text{—}240^\circ$ (decomp.)], 3-morpholino-4-hydroxy-, m.p. $185\text{—}186^\circ$ [hydrochloride, m.p. $238\text{—}240^\circ$ (decomp.)]; *Ac* derivative hydrochloride, m.p. $203\text{—}204^\circ$ (decomp.), 4-hydroxy-3-morpholinomethyl- [hydrochloride, m.p. 173° (decomp.)], and 2-morpholino-1-hydroxy-1:2:3:4-tetrahydrophenanthrene, forms, *A* (stable), m.p. $179\text{—}180^\circ$ [hydrochloride, m.p. 245° (decomp.)]; *Ac* derivative hydrochloride, m.p. 189° (decomp.), *B*, m.p. $139\text{—}140.5^\circ$ [hydrochloride, m.p. $252\text{—}253^\circ$ (decomp.)], and *B'* (unstable; gives *A*), m.p. $153\text{—}154^\circ$ [*Ac* derivative hydrochloride, m.p. $208\text{—}210^\circ$ (decomp.)]. Eight of the alcohols (remainder not tested) have little or no analgesic action.

R. S. C.

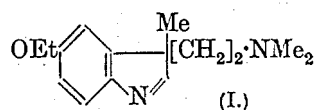
Cyanine dyes.—See B., 1938, 1274.

Synthesis and pharmacological study of heterocyclic derivatives related to aminomethylbenzodioxan. G. BENOIT and D. BOVET (Bull. Sci. Pharmacol., 1938, 40, 97—106).—Condensation of NH_2Ph with $\text{Cl}[\text{CH}_2]_2\text{N}(\text{Et})_2$ at 145° yields $\text{NHPh}[\text{CH}_2]_2\text{N}(\text{Et})_2$, b.p. $158^\circ/22$ mm. (monohydrochloride, m.p. 128°). $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ and $\text{CH}_2\text{Br-CHBr-CH}_2\text{-N}(\text{Et})_2$ in boiling COMe_2 afford diethylaminomethyltetrahydroquinoxaline, b.p. $175^\circ/3.5$ mm. (non-cryst. hydrochloride); piperidinomethyltetrahydroquinoxaline, b.p. $170\text{—}180^\circ/2.8$ mm., is obtained similarly. *Ph* aminoethyl, b.p. $176\text{—}178^\circ/28$ mm., *Ph* diethylaminoethyl, b.p. $156\text{—}158^\circ/22$ mm. (hydrochloride, m.p. $105\text{—}106^\circ$), *Ph* β -bromoethyl, b.p. $149\text{—}151^\circ/28$ mm., and *Ph* methylaminoethyl sulphide, b.p. $158\text{—}160^\circ/40$ mm. (hydrochloride, m.p. 105°), are described. 4:4'-SH- $\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-SH}$ gives 4:4'-di-(β -diethylaminoethylthiol)diphenyl (dihydrochloride, m.p. $182\text{—}183^\circ$) and 4:4'-di-(β -methylaminoethylthiol)diphenyl (dihydrochloride, m.p. 173°). With the appropriate substituted dibromopropylamine $\text{o-OH-C}_6\text{H}_4\text{-SH}$ affords diethylaminomethylbenzothioxan, $\text{C}_6\text{H}_4\text{-O} \begin{array}{c} \text{S-CH}_2 \\ \text{CH}_2\text{-O} \end{array} \text{CH-CH}_2\text{-N}(\text{Et})_2$, b.p. $202\text{—}203^\circ/35$ mm. (non-cryst. hydrochloride), and piperidinomethylbenzothioxan, b.p. $185\text{—}190^\circ/27$ mm., m.p. 108°

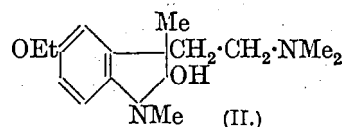
(hydrochloride, m.p. 238°). $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SH}$ gives *diethylaminomethylbenzodihydrothiazine*, $\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}>\text{CH}\cdot\text{CH}_2\cdot\text{NEt}_2$, b.p. 183—185°/4.75 mm. (non-cryst. hydrochloride), and *piperidinomethylbenzodihydrothiazine*, b.p. 202°/4.6 mm., 197°/3.2 mm. The physiological action of these compounds is discussed. H. W.

Racemisation of ephedrine and ψ -ephedrine.—See B., 1938, 1363.

Synthetic experiments with eserine. V. Constitution of *dl*-eserethole. T. KOBAYASHI (Annalen, 1938, 536, 143—163; cf. Hoshino and Kobayashi, A., 1934, 667; King *et al.*, *ibid.*, 89, 1235).—Methyl-eserethole (I), m.p. 80—81°, is identified as 5-ethoxy-



3-methyl-3-dimethylaminoethylindolenine (I). It contains 1 OEt and 2 N-Me but no active H. It is obtained from dinoreserethole with MeI in EtOH or Et₂O, from dinoreserethole benzoate with MeI or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$, or from the benzoate with MeI or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ in presence of NaOBz or NaOAc. Noreserethole or its benzoate and MeI do not give (I) according to any of these methods; the product is the original material



or the eseretholemethine base (II) or the latter exclusively. Similarly the action of $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ does not lead to (I) but to the monopicate of the methine base and the p -toluenesulphonyl derivative of (I). If the benzoate of isonoreserethole is treated with MeI in presence of NaOBz (I) is obtained in very good yield. Formation occurs still more readily when isonoreserethole methiodide, m.p. 161—162°, readily obtained from the base and MeI in Et₂O, is treated with cold dil. alkali. Thermal decomp. of the methiodide in a vac. results in 5-ethoxy-3-methylindole. Further, the methine base is formed by heating with MeI at 100° or by boiling with NaOBz-EtOH. In attempts to obtain (I) synthetically, $\text{CHMe}(\text{CO}_2\text{Et})_2$ is converted by $\text{C}_2\text{H}_5\text{Br}_2$ into *Et*₂ α -methyl- α - β' -bromoethylmalonate, b.p. 145—150°/20 mm., transformed by $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NK}$ into *Et*₂ α -methyl- α - β' -phthalimidoethylmalonate, m.p. 72—73°, or by prolonged heating with NHMe_2 in abs. EtOH at 50—55° into *Et*₂ α -methyl- $\alpha\beta'$ -dimethylaminoethylmalonate, b.p. 137—141°/14 mm. (hydrobromide, m.p. 167—168°; hydrochloride, m.p. 172°). Hydrolysis, decarboxylation, and esterification of this leads to *Et* α -methyl- γ -dimethylamino- n -butyrate, b.p. 82—84°/16 mm. (methiodide, m.p. 128—129°); the corresponding free acid, m.p. 75—76°, could not be converted into the related aldehyde. 5-Ethoxytryptaminetrimethylammonium iodide (III), m.p. 111—112°, is obtained in 93.5% yield by heating 5-ethoxytryptamine benzoate (IV) with MeI and K_2CO_3 in EtOH-H₂O at 100°. K_2CO_3 , Me_2SO_4 , and (IV) in EtOH-H₂O at 100° afford 5-ethoxytryptaminetrimethylammonium methosulphate, m.p. 181—182°. Bufotenin Et ether (V) is obtained from (III) and NH_2Ph or

$\text{NH}_3\cdot\text{EtOH}$ at 170° or from (IV) and $\text{NH}_3\cdot\text{H}_2\text{O}$ at 200°. Only bufotenin Et ether methiodide, m.p. 111—112°, could be isolated from the products of the successive action of MgEtI in $\text{C}_6\text{H}_6\cdot\text{Et}_2\text{O}$ and MeI at 100° on (V). *dl*-Eserethole is resolved by the successive application of *d*- and *l*-tartaric acid in EtOH. The following are described: *d*-eserethole *H* *d*-tartrate m.p. 173—174°, $[\alpha]_D^{25} + 115.5^\circ \pm 0.7^\circ$ in H₂O; *l*-eserethole *H* *l*-tartrate, m.p. 173—174°, $[\alpha]_D^{25} - 115^\circ \pm 0.8^\circ$ in H₂O, *dl*-eserethole *H* *dl*-tartrate, m.p. 166—167°; *d*-, m.p. 135—136°, and *l*-eserethole picrate, m.p. 135—136°; *dl*-, m.p. 137—138°, *d*-, m.p. 127—128°, and *l*-eseroline, m.p. 127—128°; *dl*-, m.p. 174—175°, *d*-, m.p. 197—198°, and *l*-isoeserine, m.p. 197—198°; *dl*-eserine salicylate, m.p. 161—162°; *d*-, m.p. 180—181°, $[\alpha]_D^{25} - 63.24^\circ \pm 0.52^\circ$, and *l*-eserine salicylate, m.p. 180—181°, $[\alpha]_D^{25} + 63.53^\circ \pm 1.61^\circ$. H. W.

Lupin alkaloids. XIII. Resolution of *dl*-lupinine. G. R. CLEMO, W. MCG. MORGAN, and R. RAPER (J.C.S., 1938, 1574—1575).—*l*-Lupinine forms a *d*-tartrate, m.p. 170°, $[\alpha]_D^{25} + 15.5^\circ \pm 0.5^\circ$ in EtOH, a *d*-camphorsulphonate, m.p. 182°, $[\alpha]_D^{25} + 22.5^\circ$, a *l*-camphorsulphonate, m.p. 184°, $[\alpha]_D^{25} - 15.3^\circ$, and a picrolonate, m.p. 191°. Octahydropyridococylcarbinol (*dl*-lupinine; cf. A., 1937, II, 355) is resolved through the tartrates, giving *l*-lupinine, identical with the natural product and *d*-lupinine, m.p. 68°, $[\alpha]_D^{25} + 19.9^\circ$. F. R. S.

Synthesis of cytisine. I. Syntheses of ethyl 3:5-dicarbethoxypyrrone-6-acetate and the corresponding pyridones. S. K. MITRA (J. Indian Chem. Soc., 1938, 15, 455—461; cf. A., 1933, 77; 1938, II, 249).— $\text{OEt}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ and $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ (I) in NaOEt at 0° afford *Et* 3:5-dicarbethoxy- α -pyrrone-6-acetate (II), m.p. 106°, converted by aq. NH_3 at 15° for 6 hr. into *Et* 2-keto-5-carboxy-3-carbethoxy-1:2-dihydropyridine-6-acetate (III), m.p. 223°. When freshly prepared the product (carboxylic acid) is sol. in aq. NaHCO_3 , but it passes quickly into the ammonium form (cf. Simonsen, J.C.S., 1908, 93, 1022).

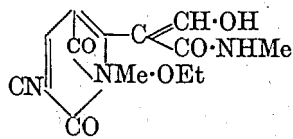
(II) and $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ in boiling EtOH for 3 hr. similarly give the β -hydroxyethylammonium salt, m.p. 189°, converted by aq. HCl into *Et* 1-(β -hydroxyethyl)-2-keto-5-carboxy-3-carbethoxy-1:2-dihydropyridine-6-acetate, m.p. 109° [SOCl_2 gives the 1-(β -chloroethyl)-derivative, m.p. 115°, the 1-OH not being attacked], which with PBr_5 in boiling Et₂O for 2 hr., and then aq. KCN, yields the 1-vinyl derivative, m.p. 130—133°.

(I) and $\text{OEt}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ similarly give *Et* 3-cyano-5-carbethoxy- α -pyrrone-6-acetate (III), m.p. 142°, converted by 26% aq. NH_3 , 30% aq. NH_2Me , and by 33% aq. NH_2Et , at 28° for 12 hr., into *Et* 2-keto-3-cyano-5-carboxy-1:2-dihydropyridine-6-acetate, m.p. 260° (decomp.), and its 1-Me (IV), m.p. 210°, and 1-Et derivative, m.p. 152°, respectively. Excess of NH_2Me affords the 6- $\text{CH}_2\cdot\text{CO}\cdot\text{NHMe}$ derivative, m.p. 285°, which with $\text{EtBr}\cdot\text{Ag}_2\text{O}\cdot\text{C}_6\text{H}_6$ (reflux; 8 hr.) affords the *Et* ether, m.p. 173°, converted by $\text{HCO}_2\text{Et}\cdot\text{Na}\cdot\text{C}_6\text{H}_6$ at 28° for 8 hr. into (V).

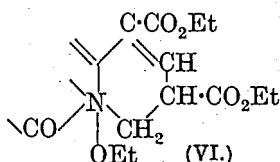
(IV) and $\text{MeI}\cdot\text{Ag}_2\text{O}\cdot\text{C}_6\text{H}_6$ (reflux 8 hr.) yield the corresponding Me ether, m.p. 123°.

Succinimide and NaOCl at 60—70° afford $\text{CO}_2\text{Et}\cdot[\text{CH}_2]_2\cdot\text{NH}_3\text{Cl}$, m.p. 58°, which with (III) in

boiling aq. NaOH-EtOH for 15 hr. gives *Et* 3-cyano-2-keto-5-carboxy-1-(*p*-carbethoxyethyl)-1:2-dihydropyrid-



(V.)



(VI.)

ine-6-acetate, m.p. 113°. The Et ether and HCO₂Et-Na-Et₂O at 28° yield (VI) (?), stable to P₂O₅ in Et₂O.

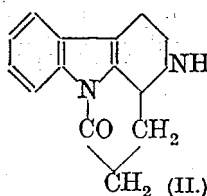
A. T. P.

β-Hydroxyphenylethylamines and their transformations. V. Condensation of hydroxyphenylethylamines with ketonic acids. G. HAHN and F. RUMFF (Ber., 1938, 71, [B], 2141—2153; cf. A., 1935, 1388).—Enolisable CO-acids, with the exception of quinolylpyruvic acid, condense readily under "physiological" conditions to tetrahydroisoquinoline-1-carboxylic acids when treated with suitable β-hydroxyphenylethylamines. Veratraldehyde, KCN, and HCl yield 3:4-dimethoxymandelonitrile, converted by NaOAc and boiling Ac₂O into acetoxy-3:4-dimethoxyphenylacetonitrile, m.p. 75—76°. Reduction (PtO₂ in AcOH containing conc. H₂SO₄) of 3:4:5-(OMe)₃C₆H₂CH:CH:NO₂ gives 3:4:5-trimethoxyphenylammonium *H* sulphate (mescaline *H* sulphate), m.p. 158°, in 83.8% yield. *iso*Vanillin, MeNO₂, and NaOH afford ω-nitro-3-hydroxy-4-methoxystyrene, m.p. 154° (yield 40.6%), catalytically reduced to 3-hydroxy-4-methoxyphenylammonium *H* sulphate, m.p. 163° [corresponding picrate, m.p. 203—204° (decomp.)]. Mescaline and conc. HCl at 130—150° give 3:4:5-trihydroxyphenylethylamine hydrochloride (I), m.p. 213.5° (corresponding picrate, m.p. 193—194°). AcCO₂H and (I) at room temp. and (preferably) *p*_H 7.0 give 6:7:8-trihydroxy-1-methyl-1:2:3:4-tetrahydroisoquinoline-1-carboxylic acid, decomp. 250° (hydrochloride, decomp. 227—228°). With the requisite CO-acid the following 6:7:8-trihydroxy-1:2:3:4-tetrahydroisoquinoline-1-carboxylic acids are obtained: with CH₂Ph·CO·CO₂H, -1-benzyl-, decomp. 239—240° (hydrochloride, complete decomp. 245° after foaming at 176°); -1-*m*-hydroxybenzyl-, decomp. 247° (hydrochloride, decomp. 268—270°); -1-*p*-hydroxybenzyl-, decomp. 258—260° after darkening (hydrochloride, decomp. 268—270°); -1-*p*-hydroxy-*m*-methoxybenzyl-, decomp. 206—230° (hydrochloride, decomp. 217—222°); -1-*m*-hydroxy-*p*-methoxybenzyl-, decomp. 259—260° (hydrochloride, decomp. 252—253°); -1-3':4'-dimethoxybenzyl-, decomp. 238° (hydrochloride, decomp. 260°); -1-3':4':5'-trimethoxybenzyl-, decomp. 241° (hydrochloride, decomp. 223—224°). The following 6-hydroxy-7-methoxy-1:2:3:4-tetrahydroisoquinoline-1-carboxylic acids are derived from β-3-hydroxy-4-methoxyphenylethylamine hydrochloride or *H* sulphate and the requisite CO-acid and NH₃: -1-methyl-, decomp. 254° (hydrochloride, decomp. 252°); -1-*m*-hydroxybenzyl-, decomp. 228° (hydrochloride, decomp. 220° after softening at 172—174°); -1-*p*-hydroxy-*m*-methoxybenzyl-, decomp. 253° [hydrochloride (also +2H₂O), decomp. 252°].

H. W.

Condensation of tryptamine with α-ketonic acids, α-ketodicarboxylic acids, and αα'-diketo-

dicarboxylic acids. G. HAHN and A. HANSEL (Ber., 1938, 71, [B], 2163—2175).—The 4-carboline system is immediately present in the product of the condensation of tryptamine (I) and AcCO₂H since it is hydrolysed under mild conditions to tetrahydroharman and 3:4:5:6-tetrahydroharman-3-carboxylic acid. The rate of condensation of (I) with 4-hydroxy-3-methoxyphenylpyruvic acid is increased by exposure to ultra-violet light and marked max. in the yield are observed in almost neutral and strongly acidic solutions. Condensation of (I) with CO-acids occurs under other than the "physiological" conditions. When buffered solutions of the components are heated to a high temp. or their alcoholic solutions are boiled there is a separation of oily matter. Action occurs much more rapidly and with equally good yield at *p*_H 1; the pptd. acid is impure but the impurities are readily removed by MeOH. At 25° a yield of 58% is slowly attained; heating greatly accelerates the reaction but at 100° the change is accompanied by decarboxylation. *m*-Hydroxybenzylpyruvic acid and (I) thus yield 3-*m*-hydroxybenzyl-3:4:5:6-tetrahydronorharman, m.p. 220—221° (decomp.) [hydrochloride, m.p. 248—249° (decomp.); methiodide, decomp. 197—198°; picrate, m.p. 198—200° (decomp.)], also obtained by the action of 12*N*-HCl at room temp. on 3-*m*-hydroxybenzyl-3:4:5:6-tetrahydronorharman-3-carboxylic acid. (I) and 3:4-dimethoxyphenylpyruvic acid yield 3:3':4'-dimethoxybenzyl-3:4:5:6-tetrahydronorharman-3-carboxylic acid, decomp. 230—232°. α-Ketoglutaric acid and (I) at 25° yield 3-ω-carboxyethyl-3:4:5:6-tetrahydronorharman-3-carboxylic acid, decomp. 190°.



converted by HCl in boiling MeOH into the amide (II), decomp. 149° (hydrochloride, decomp. 285°). αα'-Diketopimelic acid and (I) afford 3:3'-trimethylenedi-3:4:5:6-tetrahydronorharman hydrochloride, m.p. 278—279° [corresponding free base, decomp. 201—202°, and its picrate, m.p. 232—233° (decomp.)]. Under somewhat different conditions the product is 3:4:5:6:5':6'-hexahydro-1':2':3:4-benzonorharman-3'-carboxylic acid, decomp. 196—197° (hydrochloride, decomp. 244—246°; *Et* ester, decomp. 147°, and its hydrochloride, decomp. 134—135°).

H. W.

Synthesis of 3-alkyl-4-carbolines and 3:3'-polymethylenedi-4-carbolines. G. HAHN and H. F. GUDJONS (Ber., 1938, 71, [B], 2175—2182).—Tryptamine (I) and CH₂(CO₂H)₂ in EtOAc give tryptamine malonate, m.p. 162° (decomp.), which breaks down at 180° into (I), CO₂, and AcOH. Tryptamine succinate, m.p. 210°, passes at its m.p. into succinditryptamide, m.p. 199°, which yields greatly renified products when heated with POCl₃ in C₆H₆, PhMe, or xylene. Tryptamine adipate, m.p. 203° (decomp.), is converted at 210° into adipdityptamide, m.p. 193—194°, transformed by boiling POCl₃ into 3:3'-tetramethylenedi-5:6-dihydronorharman (hydrochloride, decomp. 306° after softening at 210°; picrate, m.p. 249°), which could not be satisfactorily hydrogenated by Na and boiling EtOH or by Tafel's method. Tryptamine pimelate gives successively

pimelditryptamide, m.p. 170—170.5°, and 3:3'-*pentamethylenedi-5:6-dihydronorharman*, m.p. 210° (decomp.) after softening at 200° [hydrochloride, m.p. 278° (decomp.) after softening at 270°], which appears indifferent to Na and boiling EtOH. *Tryptamine suberate* at 190° gives *suberditryptamide*, m.p. 176° after softening, which yields 3:3'-*hexamethylenedi-5:6-dihydronorharman*, m.p. 202° [hydrochloride, (+ $\frac{1}{2}$ H₂O), m.p. 261° after softening at 250°], which could not be satisfactorily hydrogenated. *Sebacitryptamide*, m.p. 165—166°, is converted by boiling POCl₃ into 3:3'-*octamethylenedi-5:6-dihydronorharman*, m.p. 210° after softening at 195° [picrate, m.p. 249° (decomp.); hydrochloride (+1.25H₂O)], which could not be hydrogenated (Adams or Tafel). Bu^oCO₂H and (I) at 200—220° give *valeritryptamide*, m.p. 88°, converted by boiling POCl₃ into the non-cryst. 3-*n-butyl-5:6-dihydronorharman* [hydrochloride, m.p. 250—251° (decomp.); picrate, m.p. 210—210.5° (decomp.)], hydrogenated (PtO₂ in AcOH) to the non-cryst. 3-*n-butyl-3:4:5:6-tetrahydronorharman* [acetate, m.p. 200°; picrate, m.p. 233° (decomp.) after softening at 230°; hydrochloride, m.p. 258° after softening at 256°]. *Palmit-tryptamide*, m.p. 110°, gives 3-*n-pentadecyl-5:6-dihydronorharman* (hydrochloride, m.p. 150—150.5°), reduced (PtO₂ in MeOH) to 3-*n-pentadecyl-3:4:5:6-tetrahydronorharman*, m.p. 82—83° (hydrochloride, m.p. 243°). Stearic acid and (I) at 160° yield *stearitryptamide*, m.p. 103°, whence 3-*n-heptadecyl-5:6-dihydronorharman* hydrochloride, m.p. 136°, and 3-*n-heptadecyl-3:4:5:6-tetrahydronorharman* hydrochloride, m.p. 236—237° after softening at 233°.

H. W.

Synthesis of 1-alkylisoquinolines and 1:1'-polymethylenediisoquinolines. G. HAHN and H. F. GUDJONS (Ber., 1938, 71, [B], 2183—2191).—Homoveratrylamine (I) and (CH₂-CO₂H)₂ at 220° yield *succindihomoveratrylamide*, m.p. 171°, which could not be satisfactorily cyclised with POCl₃ alone or in presence of C₆H₆, PhMe, or xylene in presence or absence of air. Similarly at 180—200° glutaric acid and (I) afford *glutardihomoveratrylamide*, m.p. 131.5° (yield, 95.5%), which with POCl₃ gives a non-cryst. base, hydrogenated to a viscous oil. *Adipdihomoveratrylamide*, m.p. 169°, is rapidly cyclised by boiling POCl₃ to 1:1'-*tetramethylenedi-6:7-dimethoxy-3:4-dihydroisoquinoline*, m.p. 245° (yield 80%) [hydrochloride, m.p. 171°; picrate, m.p. 250°]; this is hydrogenated, very slowly by Na and EtOH, preferably catalytically (PtO₂ in MeOH), to 1:1'-*tetramethylenedi-6:7-dimethoxy-1:2:3:4-tetrahydroisoquinoline*, m.p. 228° [hydrochloride, m.p. 252° (decomp.)]. *Pimeldihomoveratrylamide*, m.p. 140°, gives 1:1'-*pentamethylenedi-6:7-dimethoxy-3:4-dihydroisoquinoline*, m.p. 140° [hydrochloride, m.p. 229° (decomp.); picrate, m.p. 222° (decomp.)], hydrogenated (Adams) to 1:1'-*pentamethylenedi-6:7-dimethoxy-1:2:3:4-tetrahydroisoquinoline* hydrochloride, m.p. 233°. *Suberdihomoveratrylamide*, m.p. 157°, yields 1:1'-*hexamethylenedi-6:7-dimethoxy-3:4-dihydroisoquinoline*, m.p. 92° (picrate, m.p. 225°; hydrochloride, m.p. 116° after softening at 100° and, after re-solidification, m.p. 212°), which is hydrogenated to 1:1'-*hexamethylenedi-6:7-dimethoxy-*

S (A., II.)

1:2:3:4-tetrahydroisoquinoline dihydrochloride dihydrate, m.p. 254°. 1:1'-*Heptamethylenedi-6:7-dimethoxy-3:4-dihydroisoquinoline*, m.p. 140° [hydrochloride, m.p. 163° (decomp.); picrate, m.p. 198°], is derived from *azeladihomoveratrylamide*, m.p. 148°; it is converted into 1:1'-*heptamethylenedi-6:7-dimethoxy-1:2:3:4-tetrahydroisoquinoline dihydrochloride dihydrate*, m.p. 225—227° (decomp.). *Sebacdihomoveratrylamide*, m.p. 150°, affords 1:1'-*octamethylenedi-6:7-dimethoxy-3:4-dihydroisoquinoline*, m.p. 114° after softening at 100° [hydrochloride, m.p. 180° (decomp.); picrate, m.p. 188—189°], whence 1:1'-*octamethylenedi-6:7-dimethoxy-1:2:3:4-tetrahydroisoquinoline dihydrochloride dihydrate*, m.p. 248°. Palmitic acid and (I) yield *palmitihomoveratrylamide*, m.p. 93° (99% yield), transformed by boiling POCl₃ into 1-*n-pentadecyl-3:4-dihydroisoquinoline*, m.p. 74°, the hydrochloride of which appears to be very readily hydrolysed by H₂O. It is reduced (PtO₂) to 1-*n-pentadecyl-1:2:3:4-tetrahydroisoquinoline*, m.p. 65° after softening at 60° (hydrochloride, m.p. 158°).

H. W.

Synthesis of 5:6:3:14-tetrahydroxybyrinine. G. HAHN and A. HANSEL (Ber., 1938, 71, [B], 2192—2197; cf. A., 1935, 1388).—The yield of hexadehydrohimbol hydrochloride obtained by the action of CH₂O on 3-*m*-hydroxybenzyl-3:4:5:6-tetrahydronorharman hydrochloride increases somewhat as the proportion of CH₂O increased from 1 mol. to 8 mols. 3-3'-Methoxy-4'-hydroxybenzyl-3:4:5:6-tetrahydronorharman hydrochloride [corresponding base, m.p. 210—211° (decomp.), and its picrate, m.p. 134—136° (decomp.)] is transformed by CH₂O into 17-methoxy-18-hydroxy-5:6:13:14-tetrahydroxybyrinine (+1H₂O), m.p. 224—225° (decomp.) [hydrochloride, decomp. 254—256°; picrate, m.p. 185—186° (decomp.)]. 3-3':4'-Dimethoxybenzyl-3:4:5:6-tetrahydronorharman hydrochloride [corresponding base, m.p. 98° (decomp.), its picrate, m.p. 134—135° (decomp.), and methiodide, decomp. 176°] is condensed to 17:18-dimethoxy-5:6:3:14-tetrahydroxybyrinine hydrochloride, m.p. 254—255° (decomp.) after softening at 250° [corresponding base, decomp. 249—250°, and its picrate, m.p. 173—174° (decomp.)]. 3-Benzyl-3:4:5:6-tetrahydronorharman, m.p. 120—121° (decomp.) [picrate, m.p. 180° (decomp.)], does not appear to condense with CH₂O.

H. W.

Dimorphism of coralydine. G. HAHN and H. J. SCHULS (Ber., 1938, 71, [B], 2135—2140).—The α- (I) and β- (II) -coralydine obtained by Pictet *et al.* (A., 1913, i, 1224) by condensing MeCHO with tetrahydropapaverine are not isomeric racemic forms due to the presence of two unlike asymmetric centres but dimorphous varieties as observed by Hahn and Kley (A., 1937, II, 265) in the case of norcoralydine and by Bersch *et al.* (*ibid.*, 311) in those of tetrahydroberberine and canadine. (I) has m.p. 148° whereas (II) has m.p. <100°, is very unstable, and immediately becomes transformed into (I). Their derivatives and their transitions are as follows: hydrochlorides, α (III), m.p. 254° ⇌ β (IV), m.p. 229—231°; hydrobromides, α-, m.p. 231—233° → β-, m.p. 219—221°; hydriodides, α (V), m.p. 230—231° ⇌ β (VI), m.p. 218—219°; picrates, α, m.p. 134° ← β,

m.p. 118—121°. The position of the equilibrium between (III) and (IV) depends on the solvent and may be shifted in either direction by taking advantage of the more sparing solubility of (III) in H_2O and of (IV) in MeOH . Similarly crystallisation of either hydriodide from H_2O gives (VI) as solid phase whilst (V) is obtained if the material is cryst. from MeOH .

H. W.

Benzoyloxyalkyl and hydroxyalkyl ethers of cinchona alkaoids.—See B., 1938, 1366.

Strychnine and brucine. XXXVII. Conversion of dihydrostrychnidine-*D* into dihydrostrychnidine-*A*. O. ACHMATOWICZ and R. ROBINSON. XXXVIII. Exhaustive methylation of *N*(b)-methylchanodihydronostrychnidine and its dihydro-derivative. O. ACHMATOWICZ. XXXIX. Final stages of the Hofmann degradation of dihydrostrychnidine-*A*. Elimination of trimethylamine and isolation of *desazastrychnidine-b*. O. ACHMATOWICZ and C. DYBOWSKI. XL. Hofmann degradation of dimethyl-*desbrucidine*. O. ACHMATOWICZ and C. DYBOWSKI (J.C.S., 1938, 1467—1471, 1472—1483, 1483—1488, 1488—1489).—XXXVII. The *des-base-D* (A., 1934, 788) reduced with H_2 (Pd) gives methyl-dihydrostrychnidinium-*A* iodide, after addition of NaI . The implications of this are discussed. Thermal decomp. of methyl-dihydrobrucidinum-*d* chloride affords *dihydrobrucidine-D*, m.p. 197—199°.

XXXVIII. *N*(b)-Methylchanodihydronostrychnidine forms a *methiodide*, m.p. 208—210°, and *dimethiodide*, and the decomp. of the metho- and dimetho-salts of this compound with NaOMe gives a mixture of exactly the same substances, separated by a chemical method: methylchanodihydronostrychnidine, $\text{C}_{22}\text{H}_{28}\text{ON}_2$, m.p. 143—144°, *N*(b):*N*(b)-dimethyl-*desbisnostrychnidine* (I), $\text{C}_{23}\text{H}_{30}\text{ON}_2$, m.p. 113—114° [*methiodide*, m.p. 310—312°; *methochloride* (+ $7\text{H}_2\text{O}$), m.p. 235—237°; *methosulphate*, m.p. 227—229°; *dimethiodide* (+ H_2O), m.p. 273—275°; *dimethochloride* (+ $3\text{H}_2\text{O}$), m.p. 242—244°], *N*(b):*N*(b)-dimethyl-*desneostrychnidine* (II), $\text{C}_{23}\text{H}_{30}\text{ON}_2$, m.p. 73—74° [*methiodide*, m.p. 263—267°; *methochloride* (+ H_2O), m.p. 271—273°], and *methoxy-N*(b):*N*(b)-dimethyl-dihydrochanodihydrobisnostrychnidine (III), $\text{C}_{24}\text{H}_{32}\text{O}_2\text{N}_2$, m.p. 129—130°. Catalytic reduction of (I) gives a H_4 -derivative, isolated as the *methiodide*, m.p. 261—263°. Similar reduction of (III) affords a mixture of two stereoisomeric H_2 -bases, *methoxy-N*(b):*N*(b)-dimethyl-dihydrochanotetrahydrostrychnidine (IV), m.p. 131—132°, and the *allo-compound*, m.p. 113—114°. De-comp. of *N*(b)-methyl-dihydrochanodihydrostrychnidine *dimethiodide* with NaOMe yields a mixture of methyl-dihydrochanodihydrostrychnidine, $\text{C}_{22}\text{H}_{28}\text{ON}_2$, m.p. 177—178°, *N*(b):*N*(b)-dimethyl-*desdihydrostrychnidine-D*, $\text{C}_{23}\text{H}_{32}\text{ON}_2$ (*methiodide*, m.p. 299—301°), *N*(b):*N*(b)-dimethyl-*desdihydrobisnostrychnidine*, $\text{C}_{23}\text{H}_{32}\text{ON}_2$ (*methiodide*, m.p. 177—178°), and (IV). The dimethochloride of (I) and NaOMe give NMe_3 , *desazastrychnidine-a methiodide*, $\text{C}_{22}\text{H}_{26}\text{ONI}, 0.5\text{H}_2\text{O}$, m.p. 154—155°, and the -*b methiodide* (+ H_2O), m.p. 104—105°. Catalytic hydrogenation of *N*(b)-methylchanodihydronostrychnidine yields two stereoisomeric bases, *N*(b)-methyl-dihydrochanodihydrostrychnid-

ine, m.p. 177—178°, and the *allo-compound*, m.p. 117—118°. The changes which involve ring-fission and shifting of the double bond are discussed.

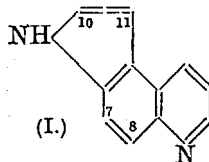
XXXIX. The *des-base-D* is methylated to a mixture of *allo-N*(b)-methyl-*desdihydrostrychnidine dimethiodide*, m.p. 274—275°, and the normal *dimethiodide*, m.p. 214—216°. The dimethochloride with NaOMe gives a mixture of the *des-base-D*, dimethyl-*desneostrychnidine*, *N*(b):*N*(b)-dimethyl-*desstrychnidine* (V), $\text{C}_{23}\text{H}_{30}\text{ON}_2$, m.p. 156—157° (*methiodide*, m.p. 244—246°), and other substances. Hydrogenation (Pd-C) of (V) affords *dihydrodimethyl-*desstrychnidine-D**, m.p. 126—127° (*methiodide*, m.p. 244—246°), and the H_4 -derivative (*methiodide*, m.p. 278—280°). The *dimethiodide*, m.p. 219—221°, is converted into the dimethochloride, which with NaOMe yields NMe_3 , dimethyl-*desstrychnidine-D*, *desazastrychnidine-b*, m.p. 109—110°, and *desazastrychnidine-a*. The formulæ for these compounds are discussed.

XL. *N*(b):*N*(b)-Dimethyl-*desbrucidine* (VI) is reduced catalytically to *tetrahydrodimethyl-*desbrucidine**, m.p. 135—136° (*methiodide*, m.p. 282—284°). The dimethochloride, prepared from *N*(b):*N*(b)-dimethyl-*desbrucidine dimethiodide* (+ $2\text{H}_2\text{O}$), m.p. 251—253°, gives (NaOMe) NMe_3 , (VI), and *desazabrucidine*, m.p. 133—134°, a very feeble base, containing 3 unsaturated linkings.

F. R. S.

Strychnos alkaloids. XX. Synthesis of 5:6-pyrroquinoline and certain derivatives. H. WIELAND and L. HORNER (Annalen, 1938, 536, 89—97).—6-Nitroquinoline is reduced (SnCl_2 and HCl) to 6-aminoquinoline, m.p. 114°, which is diazotised and then converted by SnCl_2 and HCl into 6-hydrazinoquinoline; the *hydrochloride* of this is transformed by AcCO_2H in boiling H_2O into the 6-quinolylhydrazone of pyruvic acid, the *hydrochloride*, m.p. 182° (decomp.), of which is converted by boiling $\text{EtOH-H}_2\text{SO}_4$ into the 6-quinolylhydrazone of *Et pyruvate*, m.p. 101°. This passes at 220—230° into CO_2 , EtOH , and 5:6-(? 6:7-) pyrroquinoline (I), m.p. 165° [*hydrochloride*, m.p. 273° (decomp.)], the ethereal solution of which has a blue fluorescence in sunlight or in ultra-violet light; it is reduced by Na and boiling EtOH to the non-cryst. *tetrahydropyrroquinoline*

(*hydrochloride*, m.p. 273°, after becoming brown-red at about 260°). $m\text{-C}_6\text{H}_4\text{Et-NHAc}$, b.p. 187°/14 mm., m.p. 33—34° (lit. m.p. 24—25°), is nitrated and then hydrolysed to 4:1:5- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Et-NH}_2$, transformed (Skraup) into 6-nitro-7-ethylquinoline, m.p. 86—87° after softening at 70°, which gives successively 6-amino-7-ethylquinoline (II), m.p. 109—111° (*hydrochloride*), 6-hydrazino-7-ethylquinoline (III) (*hydrochloride*), and α -ketovaleric acid 7-ethyl-6-quinolylhydrazone, m.p. 200° (decomp.). This is transformed by ZnCl_2 at 210—260° into 7:11-diethylpyrroquinoline, m.p. 195° (*hydrochloride*), which is not identical with vomipyrine obtained from vomicine. Diazotisation followed by treatment with Na_2SnO_2 converts (II) into 7-ethylquinoline, b.p. 74°/14 mm., oxidised by $\text{KMnO}_4\text{-H}_2\text{SO}_4$ to quinoline-7-carboxylic acid. AcCO_2H and (III) give the corresponding *hydrazone*, m.p. 203°, converted into the *Et ester*, m.p. 92°, whence 7-ethylpyrroquino-



line, m.p. 145°. 11-Ethylpyrroquinoline has m.p. 168°.

Strychnos alkaloids. CI. Behaviour of the red ortho-quinones from brucine and dihydrobrucine. H. LEUCHS, H. SEEGER, and K. JAEGER (Ber., 1938, 71, [B], 2023—2030).—Brucine is converted by 5N-HNO₃ at -5° into the red o-quinone (yield 80%), also obtained with CrO₃ in 5N-H₂SO₄ and isolated as the perchlorate, C₂₁H₂₀O₄N₂·HClO₄. It gives a semicarbazone [perchlorate (I)]. At 30—40° it gives a yellow-green oxime perchlorate, whereas at 80° it affords the violet oxime hydrate isolated as the perchlorate (II), C₂₁H₂₃O₅N₂·HClO₄. Reduction of (I) by Sn and 12N-HCl at 0—20° gives the aminohydroxystrychnine double salt, C₂₁H₂₃O₃N₃·2HCl·SnCl₂, also obtained by reduction of (II). This is transformed by Ac₂O and NaOAc at 100° into the Ac₃ derivative of aminohydroxystrychnine (perchlorate), hydrolysed by N-NaOH at 20° to the Ac₁ derivative (perchlorate). With Zn dust and N-HClO₄ followed by 3% H₂O₂ (II) gives the oxazine dye, (?) C₄₂H₄₁O₆N₅. Similarly, dihydrobrucine gives a red quinone (III), C₂₁H₂₂O₄N₂, m.p. 255° (decomp.) after becoming discoloured at 200° (perchlorate; Ac₂ derivative perchlorate). (III) yields a semicarbazone, C₂₂H₂₅O₄N₅ (perchlorate; hydrochloride), and an oxime hydrochloride. Hydrogenation (PtO₂) of the last substance followed by passage of SO₂ through the solution leads to aminohydroxydihydrobrucine, m.p. about 308° (decomp.) (hydrochloride, m.p. >300°; hydroperchlorate). It is reduced by Zn dust and Ac₂O at 0—30° to the diacetyl hydrate, C₂₅H₃₁O₆N₃ (perchlorate) hydrolysed (N-NaOH) to the corresponding Ac₁ derivative, m.p. about 298° (decomp.) (perchlorate), and by Zn and mineral acid to the compound, C₄₂H₄₅O₆N₅ (perchlorate).

H. W.

Veratrine alkaloids. IV. Degradation of cevine methiodide. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1938, 125, 625—634).—Cevine methiodide, C₂₇H₄₅O₈N·MeI, was converted into the betaine, C₂₈H₄₅O₈N (de-N-methylcevine) (hydrochloride + EtOH, m.p. 242°, + MeOH, m.p. 248—250°), by heating with aq. KOH in N₂. This was distilled with soda-lime in H₂ and the distillate hydrogenated. Of the resulting syrup a fraction of b.p. 208—209° gave a cryst. methiodide, C₉H₁₉ON·MeI, m.p. 242—243°, [α]_D²⁰ +14.5° in EtOH, and thence by Hofmann degradation the tert. methyl iodide, C₁₁H₂₄ONI, m.p. 132—133°, [α]_D²³ -16° in H₂O. Hydrogenation of cevine with either Raney Ni or Na and boiling BuOH gave a base, C₂₇H₄₅O₈N, m.p. 263—265°, and a small quantity of a base, C₂₇H₄₅O₇N, m.p. 284—287°, both optically active.

T. F. D.

Minor alkaloids of Duboisia myoporoides. II. Poroidine and isoporoidine. G. BARGER, W. F. MARTIN, and W. MITCHELL (J.C.S., 1938, 1685—1690).—Base Z (cf. A., 1938, II, 34) has [α]_D²⁰ +2.5° in EtOH, forms an oxalate, m.p. 296—297°, and a hydrobromide, m.p. 219—220°, [α]_D²⁰ +2.9° in H₂O, can be racemised indirectly, and on hydrolysis [Ba(OH)₂] gives nortropine and a mixture (~10:1) of Bu^cCO₂H and d-α-methylbutyric acid. Tiglyl chloride and nortropine hydrochloride afford tiglylnortropine, isolated as the hydrobromide, m.p. 241—242°, reduced (H₂-PtO₂) to

S* (A., II.)

dl-α-methylbutyrylnortropine hydrobromide (I), m.p. 201—202° (oxalate, m.p. 296—297°), not identical with base Z hydrobromide. Bu^cCOCl and nortropine hydrochloride yield isovalerylnortropine hydrobromide, m.p. 224—225° (oxalate, m.p. 301—302°), which, when mixed with (I), gives a product identical with base Z hydrobromide. An indirect separation of base Z has been achieved by hydrolysis (KOH), followed by fractional pptn. of the Ag salts of the acids from aq. solution; Bu^cCO₂H has been isolated. Reduction (H₂-PtO₂) of tiglylnortropine hydrobromide gives dl-α-methylbutyrylnortropine hydrobromide, m.p. 210°. The p-phenacyl esters of the butyric and valeric acids are described. The conclusion is reached that base Z is a mixture of much isovalerylnortropine (poroidine) with a little d-α-methylbutyrylnortropine (isoporoidine).

F. R. S.

Alkaloids of Magnolia fuscata. N. PROSKURNINA and A. ORÉKHOV (Bull. Soc. chim., 1938, [v], 5, 1357—1360).—The C₂H₅Cl₂ extract of the leaves, moistened with aq. NH₃, of *M. fuscata* is treated with 10% H₂SO₄ and the acid extract made alkaline (aq. NH₃). Crystallisation from C₆H₆ affords magnoline, C₁₆H₁₄O(NMe)(OMe)(OH), m.p. 178—179°, [α]_D -9.6° in C₅H₅N [picrate, softens 140°, m.p. 160—162° (decomp.); picrolonate, softens 160°, m.p. 190° (decomp.)], and the more sol. magnolamine, C₁₈H₁₆O₂(NMe)(OMe)(OH), m.p. 117—119° (softens at 110°), [α]_D +111.6° in EtOH [picrate, m.p. 142—145° (decomp.); picrolonate, m.p. 163—164° (decomp.)].

A. T. P.

Application of electrodialysis to the extraction of alkaloids. I. Drugs and pharmacological preparations. R. FABRE and P. OFICJALSKI (J. Pharm. Chim., 1938, [viii], 28, 335—343; cf. A., 1938, III, 753).—Electrodialysis (0.5 amp. for 6—24 hr. depending on the nature of the electrolyte) separates alkaloids which do not readily react with the O₂ liberated at the anode. Brucine is partly destroyed if it is placed in the anodic compartment, but if it is in a third vessel which contains neither electrode, it is completely recovered. Electrodialysis is conducted with acidified (0.1N-AcOH or -H₂SO₄) cathodic fluid or one containing 40% of C₆Me₂ or EtOH, or EtOAc. The yields are consistent and better than those obtained when the pharmacopœial method of extraction is used. The process is applied to nuxvomica, quinine, ipecacuanha and several of its preps. Atropine, morphine, and cocaine are oxidised and give poor yields.

J. L. D.

Relative reactivities of organometallic compounds. XIX. Hydrogenolysis of RM compounds. II. GILMAN, A. L. JACOBY, and (Miss) H. LUDEMAN (J. Amer. Chem. Soc., 1938, 60, 2336—2338; cf. A., 1937, II, 221).—Very reactive organo-alkali compounds, MR, are reduced by H₂ at room temp. mainly to RH and MH. For MPh the relative rates of reaction in C₆H₆ are Ca < Li < Na < K < Rb < Cs; for LiR in C₆H₆ suspension the no. of hr. required for similar degrees of hydrogenolysis are R = Ph 32.2, Me 38.5, α-C₁₀H₇ 40, Bu^c 61, n-C₇H₁₅ 66, n-C₁₂H₂₅ 91, and p-C₆H₄Me 150. For NaPh the rates are different in C₆H₆ and light petroleum; in the latter the rate-controlling factor is probably the

rate of diffusion of H_2 through the liquid; in C_6H_6 it is a first-order reaction, in which $[H_2]$ is const. Pd and Pt have no significant effect on the reaction of LiPh or NaPh.

R. S. C.

Organic antimonials of therapeutic activity. G. M. DYSON (Rec. trav. chim., 1938, 57, 1016—1028).—By diazotising the appropriate amine and treating with $SbCl_3$ in HCl, the following are obtained: *p*-fluoro- (*Na* salt), *p*-iodo-, *p*-ethoxy-, 2-chloro-4-methyl-, *p*-bromo- (hydrolysed by NaOH to *p*-hydroxy-), *p*-dimethylamino-, *p*-methoxy-, *p*-carboethoxy-phenylstibinic acid, and α - and β -naphthylstibinic acid. Similar treatment of *p*- $C_6H_4AcNH_2$ yields 2:4'-diacetoazobenzene-5-stibinic acid, and of 3:4- $C_6H_3Cl_2NH_2$ yields 2:3:3':4'-tetrachloroazobenzene-5-stibinic acid. $CH_2(C_6H_4 \cdot p-NH_2)_2$ yields diphenylmethane-4:4'-distibinic acid, benzidine and dianisidine give diphenyl- and 3:3'-dimethoxydiphenyl-4:4'-distibinic acid respectively, whilst *p*- $C_6H_4(NH_2)_2$ yields benzene-*p*-distibinic acid. *p*- $NH_2 \cdot C_6H_4 \cdot SbO_3H_2$ (I) with HCl and $CSCl_2$ yields 4-thiocarbamidophenylstibinic acid. Nitration ($HNO_3-H_2SO_4$) of *m*- $CO_2H \cdot C_6H_4 \cdot SbO_3H_2$ yields 3-nitro-, reduced ($Na_2S_2O_4$) to 3-amino-5-carboxyphenylstibinic acid. Similarly, from the appropriate substituted stibinic acids are formed 3-amino-4-methoxy-, -4-bromo-, and -4-methyl-phenylstibinic acid. The *Na* salt of (I) with CS_2 yields *s*-diphenylthiocarbamide-4:4'-distibinic acid and with *m*- and *p*- $CO_2Na \cdot C_6H_4 \cdot NCS$ and *p*- $ONa \cdot C_6H_4 \cdot NCS$, yields 3- and 4-carboxy- and 4-hydroxy-*s*-diphenylthiocarbamide-4'-stibinic acid (*Na* salts) respectively. 3:5-(NO_2) $_2 \cdot C_6H_3 \cdot CO_2H$, reduced (Sn-HCl) and treated with $CSCl_2$, yields 3:5-dithiocarbamidobenzoic acid, m.p. 150°, which in aq. NaOH with (I) yields 3:5-bis-(4'-stibinic acid phenylthiocarbimido)benzoic acid (*Na* salt). *m*- and *p*- $NH_2 \cdot C_6H_4 \cdot SO_3Na$ with $CSCl_2$ yield *Na* benzenethiocarbimide-3- and -4-sulphonate respectively, which with (I) in NaOH yield *s*-diphenylthiocarbamide-4-stibinic acid-3'- and -4'-sulphononic acid respectively (*Na* salts). 1:3:5- $C_6H_3(NCS)_3$ with (I) in NaOH yields 1:3:5-tris-(phenylthiocarbimido)benzene-4':4''':4''''-tristibinic acid (*Na* salt), whilst *p*- $NCS \cdot C_6H_4 \cdot AsO_3H_2$ with (I) yields *s*-diphenylthiocarbamide-4-stibinic acid-4'-arsinic acid (*Na* salt).

J. D. R.

Protamine salts of phosphatides, with remarks on the problem of lipoproteins. E. CHARGAFF (J. Biol. Chem., 1938, 125, 661—670).—Kephalin (I) (P/N = 1/1.1) (prep. described) emulsified in H_2O is pptd. by aq. salmine sulphate. The ppt. (II) softens at 140° and slowly decomposes [(I) 84%; P/N = 1:4 or 1:5], is not emulsified in contact with H_2O , but swells to a rubber-like, elastic, S-free mass. The composition of (II) is unaltered by varying the proportions of the reactants, or by the action of dil. acids or by crystallisation. Neither lecithin (III) nor sphingomyelin reacts with salmine like (I). (II) is formed over the p_H range 1.9—11; (III) reacts only at p_H 10 and 11. At p_H < 10, salmine diminishes the stability of the (III) emulsion. (II) is probably a salt as the phosphatide has markedly acidic properties (cf. A., 1927, 227; 1931, 249) in contrast to (III) in the p_H range studied. At p_H 1.9—3.9 (I), but not (III), immediately affords a

ppt. with purified egg-albumin. The significance of these results is discussed.

J. L. D.

Composition of elastin. W. H. STEIN and E. G. MILLER, jun. (J. Biol. Chem., 1938, 125, 599—614).—The NH_2 -acid distribution in elastin agrees with Bergmann's frequency theory (A., 1937, III, 168).

E. M. W.

Distribution of the sulphur in casein, lactalbumin, edestin, and papain. (MISS) B. KASSELL and E. BRAND (J. Biol. Chem., 1938, 125, 435—443).—Analyses are given of the distribution of S in casein, lactalbumin, reduced lactalbumin, edestin, and papain and the methods employed are fully discussed. The S of casein, lactalbumin, and reduced lactalbumin can all be accounted for as cystine, cysteine, and methionine, but in edestin and in a prep. of papain a considerable proportion of the S remains undetermined.

W. O. K.

Development of protein chemistry. E. FÄRBER (J. Chem. Educ., 1938, 15, 434—444).—A review of progress.

L. S. T.

Covalent symplexes from carbohydrates and proteins. II. Compounds produced by union of lysine residues and reducing sugars. S. J. VON PRZYBYCKI and J. CICHOCKA (Biochem. Z., 1938, 299, 92—99).—Only the free NH_2 of lysine residues in proteins interacts with the terminal group of reducing sugars and the extent of interaction is not \propto the lysine content. There are great differences in stability between the symplexes produced. The compounds produced by the interaction of maltose with ovalbumin, caseinogen, and serum-albumin contain 1.1, 7, and 9% respectively of maltose. Probably only part of the free NH_2 of lysine residues of the protein takes part in the reaction. The proteins yield no compounds with sucrose. It is improbable that symplexes of this type are produced in the living organism.

W. McC.

State of combination of iron in iron-protein compounds. F. G. FISCHER and K. HULTZSCH (Biochem. Z., 1938, 299, 104—122).—When vitellin (I) is converted into vitellinic acid or subjected to tryptic or peptic digestion the "masked" Fe^{III} and PO_4^{III} accumulate in the same degradation products and when it is boiled with dil. aq. KOH Fe^{III} and PO_4^{III} are eliminated in proportions bearing a const. ratio to each other. At p_H < 1 proteins such as (I) and caseinogen or proteins "phosphorylated" with $POCl_3$ or pptd. with HPO_3 are the only ones which combine with Fe. As regards the state of combination of their Fe^{III} , Fe^{III} salts of simple phosphoric esters (Et_2 , Bu_2 , Ph , Ph_2 , dibenzyl, di-*o*-tolyl) behave like proteins which contain PO_4 . The max. amount of Fe^{III} which these esters and the PO_4 -containing proteins take up at p_H < 1 is approx. 1 Fe for each P. These results suggest that, very probably, the "masking" of Fe in proteins and nucleic acids is due to production of complex Fe^{III} salts of org. PO_4 which dissociate only slightly even in acid solution.

W. McC.

Influence of substances on the optical rotation of gelatin. VII. Rotatory dispersion of gelatin in carbamide solutions. D. C. CARPENTER and

F. E. LOVELACE (J. Amer. Chem. Soc., 1938, **60**, 2289—2294; cf. A., 1938, I, 80).—The rotatory dispersion of gelatin in aq. $\text{CO}(\text{NH}_2)_2$ at 0.5° and 40° follows a single-term Drude equation. At 40° the dispersion const. \propto the concn. of $\text{CO}(\text{NH}_2)_2$. At 0.5° a logarithmic function also affects the dispersion. $\text{CO}(\text{NH}_2)_2$ is intermediate in effect between NaCl and NaBr. The max. lowering of the dispersion const. is about two thirds of that produced by Na halides. After removal of the $\text{CO}(\text{NH}_2)_2$ by dialysis $[\alpha]$ returns to its original val., showing that "denaturation" did not occur. R. S. C.

Thiol groups in proteins. I. Ovalbumin in solutions of urea, guanidine, and their derivatives. J. P. GREENSTEIN (J. Biol. Chem., 1938, **125**, 501—513).—Determination of SH groups by means of porphyrindin gives a cysteine content of 1.0 and 1.24% for solutions in aq. $\text{CO}(\text{NH}_2)_2$ and aq. guanidine hydrochloride, respectively. The liberation of SH groups depends on the concn. of $\text{CO}(\text{NH}_2)_2$ or guanidine but not on that of the protein. Of the 6 alkali-labile S in the mol., 4 appear to belong to cysteine. The action of the solvents is discussed. E. M. W.

Laboratory columns.—See A., 1938, I, 586.

Determination of carbon and hydrogen. S. NATELSON, S. S. BRODIE and E. B. CONNER (Ind. Eng. Chem. [Anal.], 1938, **10**, 609—612; cf. A., 1938, II, 301).—An apparatus for determining C and H on 2.5—35-mg. samples is described. F. N. W.

Micro-Kjeldahl distillation apparatus.—See A., 1938, I, 640.

Kjeldahl nitrogen determination.—See A., 1938, I, 636.

Use of persulphate in determination of nitrogen without distillation.—See A., 1938, I, 582.

Determination of mercury in organic compounds. R. JACQUEMAIN and (MLE.) G. DEVILLERS (Bull. Soc. chim., 1938, [v], **5**, 1338—1340; cf. Borelli, A., 1907, ii, 816; Verdino, A., 1928, 386).—The organo-Hg compounds are decomposed by HCl-KClO_3 on the water-bath. Electrolysis with Pt anode and Ag foil cathode, immersed completely by suspending on a Pt rod, at 0.1 amp./1.5—2 v., gives complete deposition of Hg in 10 hr. A. T. P.

Micro-Zeisel method. II. Determination of alkoxy and alkimide groups. Experiences and improvements. III. Determination of alkoxy and alkimide groups in substances which are readily volatilised or decomposed with difficulty. M. FURTER (Helv. Chim. Acta, 1938, **21**, 1144—1151, 1151—1161; cf. A., 1938, II, 385).—II. Pt tetrahedra are recommended to ensure regular boiling. Solids are weighed in a long tube which can be brought to the bottom of the flask through the tube used for passage of CO_2 ; there they can readily be dissolved by $\text{Ac}_2\text{O-PhOH}$. A suitable apparatus for weighing liquids is indicated. The wash liquid, 10% $\text{Na}_2\text{S}_2\text{O}_3$ and 10% CdSO_4 containing a few particles of red P, must be freshly prepared. Only fresh HI (d 1.7) pale in colour may be used. For acetals, ethers, and esters of low b.p. from which alcohols of low b.p.

distil without reacting with the HI, an apparatus is designed in which the vapours from the customary flask pass through a second flask containing boiling HI on their way to the wash-flask. The apparatus is also useful in the determination of NAlk whereby the second flask functions as distillate receiver. A modified vessel for the absorption of alkyl iodides is described.

III. For volatile etc. substances it is recommended to use a vessel which can be sealed and heated at 135° . After the required period it is cooled in a Dewar vessel with solid CO_2 and Et_2O and then opened. It then forms the usual flask and is connected by a suitable head to the customary washing and absorbing apparatus. HI of d 1.7 should be used. If the acid of d 1.9 is employed high results are obtained even when the wash liquid contains 20% $\text{Na}_2\text{S}_2\text{O}_3$ and 20% CdSO_4 with red P. The temp. of the reaction must be $>140^\circ$; at higher temp. in presence of HI alkanes and I result from alkyl iodides, which in absence of HI are nearly stable under these conditions. H. W.

Iodometric titre of methyl alcohol. M. STRADA and C. MERLI (Annali Chim. Appl., 1938, **28**, 318—324).—Accuracy in the iodometric determination of small amounts of COME_2 in (e.g., synthetic) MeOH is obtained by having a val. of 2.5 for the ratio c.c. of 0.1N-I per c.c. of MeOH taken and by allowing the I to react with the MeOH for a time and temp. <3 hr. and 35° , respectively. F. O. H.

Determination of lower alcohols by means of the corresponding ethylene hydrocarbons. O. GRANE, B. LÖFSTRÖM, and R. WINDBLADH (Ingeniörs Vetensk. Akad. Handl., 1938, No. 147, 19 pp.).— EtOH , $\text{Pr}^\alpha\text{OH}$, Pr^βOH , and the butyl alcohols when passed over Al_2O_3 at 300° yield C_2H_4 , C_3H_6 , and C_4H_8 quantitatively; these can be determined by conversion into the corresponding bromides. The process can be applied to the analysis of mixtures of EtOH , PrOH , and $\text{Bu}^\alpha\text{OH}$; allyl alcohol and ketones should be previously removed. R. B. C.

Hydroxylamine method for determination of aldehydes and ketones. S. SABETAY (Bull. Soc. chim., 1938, [v], **5**, 1419—1422; cf. B., 1932, 960).—A standard method is advanced, and examples are given, for the oximation of aldehydes and ketones; HCl liberated from $\text{NH}_2\text{OH.HCl}$ is calc. by titration (0.5N-KOH). A. T. P.

Determination of sugars with copper solutions. J. STRAUB and D. A. MIDDELBECK (Chem. Weekblad, 1938, **35**, 743—746).—Two reactions occur in the oxidation of sugars with alkaline Cu solutions involving destruction of the sugar by the alkali and oxidation of the enol forms, which are the primary decomp. products. Both reactions lead rapidly via labile intermediate products to OH-acids which are stable to both alkalis and Cu compounds. S. C.

Elimination [and micro-determination] of amines.—See A., 1938, III, 1030.

Identification of amino-acids by means of 3:5-dinitrobenzoyl chloride. II. B. C. SAUNDERS (J.C.S., 1938, 1397—1402; cf. A., 1934, 638).—Further examples of the use of 3:5-dinitrobenzoyl

chloride (I) for identifying NH_2 -acids, peptides, etc. are given and discussed. The following are described: 3:5-dinitrobenzoylglycylglycine, m.p. 210° ; 3:5-dinitrobenzoyldiglycylglycine, m.p. 236° (decomp.); 3:5-dinitrobenzoyl- β -alanine, m.p. 202.5° ; 3:5-dinitrobenzamidohexanoic acid, m.p. $129\text{--}131^\circ$; 3:5-dinitrobenzoylsarcosine + H_2O , m.p. 153.5° ; 3:5-dinitrobenzoyl-dl-proline, m.p. 217° ; N-3:5-dinitrobenzoyl-dl-serine + H_2O , m.p. $94\text{--}95^\circ$; 3:5-dinitrobenzoylhistidine + H_2O , m.p. 189° (Na salt); bis-(3:5-dinitrobenzoyl)-d-lysine, m.p. 115° (+ $2\text{H}_2\text{O}$, m.p. 169° , softening about 160° ; Na salt + $2\text{H}_2\text{O}$); Na dinitrobenzoyltaurate; Na 3:5-dinitrobenzoylsulphanilate + $3\text{H}_2\text{O}$; 3:5-dinitrobenzoylanthranilic acid, m.p. 278° , softens at 269° (Na salt); m-, m.p. 270° , and p-, m.p. $>290^\circ$; -3:5-dinitrobenzamidobenzoic acid. Glyoxaline, like $\text{C}_5\text{H}_5\text{N}$, converts (I) into its anhydride. Lactic acid does not react with (I) in presence of NaOH. 3:5-Dinitrobenzoylglycine is hydrolysed by 70% H_2SO_4 at the b.p. in about 5 min. (cf. *loc. cit.*). H. G. M.

Physico-chemical methods of analysing binary mixtures of benzene, toluene, and xylene. K. HRADSKY (Chem. Obzor, 1936, 11, 129—131, 162—166; Chem. Zentr., 1937, i, 140).—A titration method based on the vol. of a solvent (MeOH, EtOH, AcOH) necessary to clarify a suspension of the hydrocarbons in H_2O is described. A. H. C.

Quantitative separation of carotenoids and vitamin-A.—See A., 1938, III, 1024.

Potentiometric studies in diazotisation. Determination of aromatic amines. B. SINGH and G. AHMED (J. Indian Chem. Soc., 1938, 15, 416—420; cf. Müller and Dachselt, A., 1926, 314).— $\text{C}_6\text{H}_4\text{R}\cdot\text{NH}_2$ ($\text{R} = p\text{-Cl}$, o -, m -, and $p\text{-NO}_2$, o - and $p\text{-CO}_2\text{H}$, $p\text{-SO}_3\text{H}$), 5:2:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2$, and 2:4:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{NH}_2$ are determined quantitatively by potentiometric titration of solutions in HCl against standard aq. NaNO_2 at $\pm 20^\circ$ (Pt electrode in amine solution, coupled with saturated calomel electrode). The e.m.f. rises steadily to the equiv. point, when a sharp rise in potential occurs. Curves are drawn. A. T. P.

Colorimetric determination of cholesterol and its esters by the Liebermann-Burchard reaction. E. C. NOYONS (Biochem. Z., 1938, 298, 391—395).—The results obtained by the method (with the use of the step photometer) are trustworthy only after any cholesteryl ester present has been hydrolysed. W. McC.

Detection of small amounts of phenolphthalein in the presence of emodin and of chrysophanic acid. E. H. MAECHLING (Ind. Eng. Chem. [Anal.], 1938, 10, 586).—0.5—1.0 g. of the powdered sample suspended in 20 c.c. of aq. NaHCO_3 is extracted thrice with Et_2O (25, 15, and 15 c.c.) and the residue after removal of the solvent from the combined extracts is dissolved in 20 c.c. of 10% aq. KOH and subsequently oxidised by successive additions of 30% aq. H_2O_2 with gentle heating. After cooling, filtration, and acidification with dil. H_2SO_4 the solu-

tion is again extracted thrice with Et_2O , and the combined extracts are washed and evaporated to dryness. The residue is heated ($180\text{--}200^\circ$ for 20 min. or boiled for 5 min.) with an excess of resorcinol, cooled, and the mixture dissolved in 5 c.c. of aq. KOH to give a green fluorescence with amounts of phenolphthalein $>5\text{--}10$ μg . F. N. W.

Pyridine-3-carboxyldiethylamide (Coramine). H. J. VAN GIFFEN (Pharm. Weekblad, 1938, 75, 1121—1123).—A sample of nicotindethylamide (99.7%), m.p. $18\text{--}24^\circ$, d_{20}^{25} 1.0642, n_D^{20} 1.5250, p_H 6.1, gave ppts. with Nessler's reagent, 5% HgCl_2 , tannin, and KBiI_4 (brick-red) but not with I, picric acid, or KHgI_3 and practically no blue coloration was formed with CuSO_4 . S. C.

Determination of tyrosine, tryptophan, and cystine by means of the step photometer. Application to Folin and Marenzi's colorimetric method. P. BALINT (Biochem. Z., 1938, 299, 133—136).—The application of photometric procedure to the determination, in 50—60 mg. of protein, of tyrosine and tryptophan by the method of Folin and Marenzi (A., 1929, 1093) and of cystine + cysteine by Lugg's method (A., 1933, 266) is described. Standard solutions are not required. W. McC.

Potentiometric characterisation of thionol.—See A., 1938, 625.

Styphnic and picric acids in the microchemistry of alkaloids. I. A. OLIVERIO (Annali Chim. Appl., 1938, 28, 353—363).—Data are given for the crystal habits, solubility, and m.p. of the picrates and styphnates of atropine, brucine, quinine, cocaine, codeine, morphine, and strychnine. Priority over Kofler and Müller (A., 1937, II, 314) is claimed and some discordancies between the two sets of data are indicated. F. O. H.

Chromatography of opium alkaloids. G. R. LEVI and F. CASTELLI (Gazzetta, 1938, 68, 459—470).—The chromatographic adsorption of morphine (I), codeine (II), narcotine (III), and papaverine (IV) from C_6H_6 on to the decolorising earth "Vas." (Società del Caffaro), under 1.8 atm., is studied, in ultra-violet light, both with single and with mixed alkaloids. From the latter, (I) is separated at the top, and (IV) at the bottom; intermediate layers contain first (I), (II), and (III), then (II) and (III), followed by (II), (III), and (IV). E. W. W.

Silver in microchemical reactions. J. P. L. VILLAMIL (Arch. Med. Legal, 1933, 6, 358—365).—Various alkaloids and glucosides give cryst. ppt. with Ag_2CO_3 in NH_3 . S. O.

Determination of methionine, cysteine, and sulphate in proteins after hydrolysis with hydriodic acid. (Miss) B. KASSELL and E. BRAND (J. Biol. Chem., 1938, 125, 145—159).—Baernstein's method (A., 1936, 1282) for determining S-containing NH_2 -acids and SO_4 is improved. Results are detailed for cryst. egg-albumin, lactalbumin, and casein, all the S of which is accounted for by cysteine, cystine, and SO_4 . R. S. C.